
Effect of chemical structure and composition of the resin phase on mechanical strength and vinyl conversion of amorphous calcium phosphate-based composites

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Abstract: The mechanical properties of recently developed bioactive, antidemineralizing/remineralizing, amorphous calcium phosphate (ACP)-based composites need improvement. The objective of this study was to elucidate the effect of structure and composition of resins on the biaxial flexure strength (BFS) and the degree of conversion (DC) of composites attained after photo-polymerization. Two series of 2,2-bis[p-(2'-hydroxy-3'-methacryloxypropoxy)phenyl]propane (Bis-GMA)/triethylene glycol dimethacrylate (TEGDMA)/X (X being a neutral or acidic comonomer) ternary resins were prepared and mixed with a mass fraction of 40% of zirconia-hybridized ACP. Both unfilled copolymers and their composites were evaluated for BFS (dry and wet specimens after 2 weeks of immersion in buffered saline) and for DC (after 24 h at 23°C). It was found that for the neutral X monomers, no correlation

existed between the hydrophobic/hydrophilic character of the X monomer and the BFS values of the immersed composites. A flexible monomethacrylate yielded copolymers and composites with the highest DC. For the resins utilizing the acidic comonomers, methacrylic acid and mono-4-(methacryloyloxy)ethyltrimellitate (4MET), dry composites with improved BFS values were obtained. 4MET composites exhibited the least loss of strength of all the ternary resin ACP materials. The effect of acidic X on DC was most pronounced for maleic acid copolymers. © 2004 Wiley Periodicals, Inc. * J Biomed Mater Res 68A: 763–772, 2004

Key words: amorphous calcium phosphate; biaxial flexure strength; degree of vinyl conversion; ternary methacrylate resins

INTRODUCTION

Amorphous calcium phosphate (ACP) is a unique form of calcium phosphate (CP) that lacks the long-range, atomic scale order of crystalline CPs.¹ The possible role that ACP may play as a precursor in the formation of biological apatite (Ap)—the structural prototype of the mineral component of bone and teeth—places it in the mainstream of CP chemistry. ACP's relatively high aqueous solubility and its ready

conversion to Ap make ACP suitable as a remineralizing agent.

We have developed unique bioactive composites based on ACP as a filler phase for polymer matrices derived from the ambient polymerization of typical dental monomers, for example, a blend of 2,2-bis[p-(2'-hydroxy-3'-methacryloxypropoxy)phenyl]propane (Bis-GMA), triethylene glycol dimethacrylate (TEGDMA) and 2-hydroxyethyl methacrylate (HEMA).^{2,3} Both the physicochemical data^{4,5} and the results of *in vitro* testing⁶ showed that ACP composites in such matrices release calcium and phosphate ions in a manner that effectively "buffer"-free calcium and phosphate ion activities and, in turn, maintain the desired state of supersaturation with respect to tooth mineral. Because the release of calcium and phosphate ions occurs in a sustained manner that may be conducive to Ap formation, these composites offer a promising antidemineralization/remineralization tool in not only preventing the formation of new lesions, but also in actively repairing existing or incipient lesions. The variety of polymeric forms of ACP broadens the dental applicability of ACP beyond uses that have already been proposed, such as

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TABLE I
Monomers and Photoinitiators Employed in Resin Formulations

Component	Chemical Name	Acronym	Manufacturer
Base monomers	2,2-bis[p-(2'-hydroxy-3'-methacryloxypropoxy) phenyl] propane	Bis-GMA	Esstech, PA, USA
Hydrophilic monomers	triethylene glycol dimethacrylate	TEGDMA	Esstech, PA, USA
	2-hydroxyethyl methacrylate	HEMA	Esstech, PA, USA
	2-methoxyethyl methacrylate	MEMA	Aldrich, WI, USA
	di(ethyleneglycol)methyl ether methacrylate	DEGMEMA	Aldrich, WI, USA
	glyceryl monomethacrylate	GLMA	BiMAX, MD, USA
Acidic, surface-active monomers	glyceryl dimethacrylate	GDMA	Esstech, PA, USA
	vinyl phosphonic acid	VPA	Aldrich, WI, USA
	methacrylic acid	MA	Aldrich, WI, USA
	maleic acid	MaA	Aldrich, WI, USA
	mono-4-(methacryloyloxy) ethyltrimellitate	4MET	Prof. Nakabayashi, Japan
Component of photoinitiator system	camphorquinone	CQ	Aldrich, WI, USA
	ethyl-4-N, N-dimethylaminobenzoate	4EDMAB	Aldrich, WI, USA
	phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide	PbTMBPO	Aldrich, WI, USA

topical gels, toothpastes and/or mouthrinses,⁷ or sugar-free gums.⁸

The overall mechanical properties of these anti-demineralizing/remineralizing composites are inferior to conventional, bioinert, silanized glass-filled dental composites. This is to be expected, because the usual glass or ceramic fillers that constitute the discontinuous phase of polymeric dental composites are considerably stronger than the porous ACP. Additionally, by virtue of their silane-derived interfacial phase, the glass or ceramic fillers are chemically bound to the continuous or polymeric phase, thereby reinforcing the polymer matrix of the composite. Several recent studies^{5,9,10} were designed to better understand the relationship between mechanical strength of the composites, the chemical structure/composition of the resin, and the type of the ACP filler utilized. Although it was demonstrated that the use of hybridized ACP, such as that containing zirconium compounds in their structures in place of ACP (Zr-ACP), yielded composites with moderately improved mechanical strength,^{4,5} to further improve the strength of ACP composites it may be necessary to employ a resin that has a stronger affinity for ACP than those employed heretofore.

Thus, in this study a series of Zr-ACP composites were prepared from Bis-GMA/TEGDMA/X ternary monomer (termonomer) systems, where X is a surface-active comonomer. To assess the effect(s) of chemical structural variations of X on strength and on the extent of vinyl polymerization or degree of conversion (DC) of these potentially bioactive composites, nonfunctional and functional monomers of varying hydrophilicity were selected for this study. The functional monomers included hydroxyl- and carboxylic acid-containing monomers, and were chosen because of their ability to interact with ACP by hydrogen bonding and, in the case of the carboxylic monomers, also chemically by ion-binding reactions. One of the hypotheses of this study was that by introducing differ-

ently structured neutral or acidic comonomers into the resins improved ACP filler/resin matrices interactions would occur, leading to composites with enhanced mechanical strength. A related hypothesis was that the termonomer systems would yield materials with higher DC than a Bis-GMA/TEGDMA binary system. The level of conversion of methacrylate double bonds attained during polymerization of resin matrices can also influence the mechanical strength of composites, and can be an indicator of the potential leachability of unreacted monomeric species that can adversely affect the relative biocompatibility of ACP composites.¹¹

MATERIALS AND METHODS

Formulation of methacrylate resins

The experimental resins were formulated mainly from the commercially available dental monomers (Table I). The components of the photoinitiator system also are listed in Table I. The chemical structures of the monomers and the photocuring agents are shown in Figure 1. The indicated acronyms will be used throughout this manuscript. Bis-GMA/TEGDMA/neutral termonomer resins were generally photoactivated by the inclusion of CQ and 4EDMAB as photo-oxidant and photo-reductant, respectively. In the Bis-GMA/TEGDMA/acidic termonomer series, the diacyl phosphine oxide, PbTMBPO, was utilized as a photoinitiator because of possible storage stability problems encountered with the use of CQ and 4EDMAB and resins containing acidic monomers. Five types of Bis-GMA/TEGDMA/neutral termonomer resins (assigned BTH, BTM, BTDM, BTGM, and BTGDM), and four types of Bis-GMA/TEGDMA/acidic termonomer resins (BTVPA, BTMA, BTMAA, and BT4MET) based on 1:1 by mass mixtures of Bis-GMA/TEGDMA were formulated. The binary monomer system, Bis-GMA/TEGDMA (1:1 mass ratio) activated with CQ/4EDMAB (BT1) or

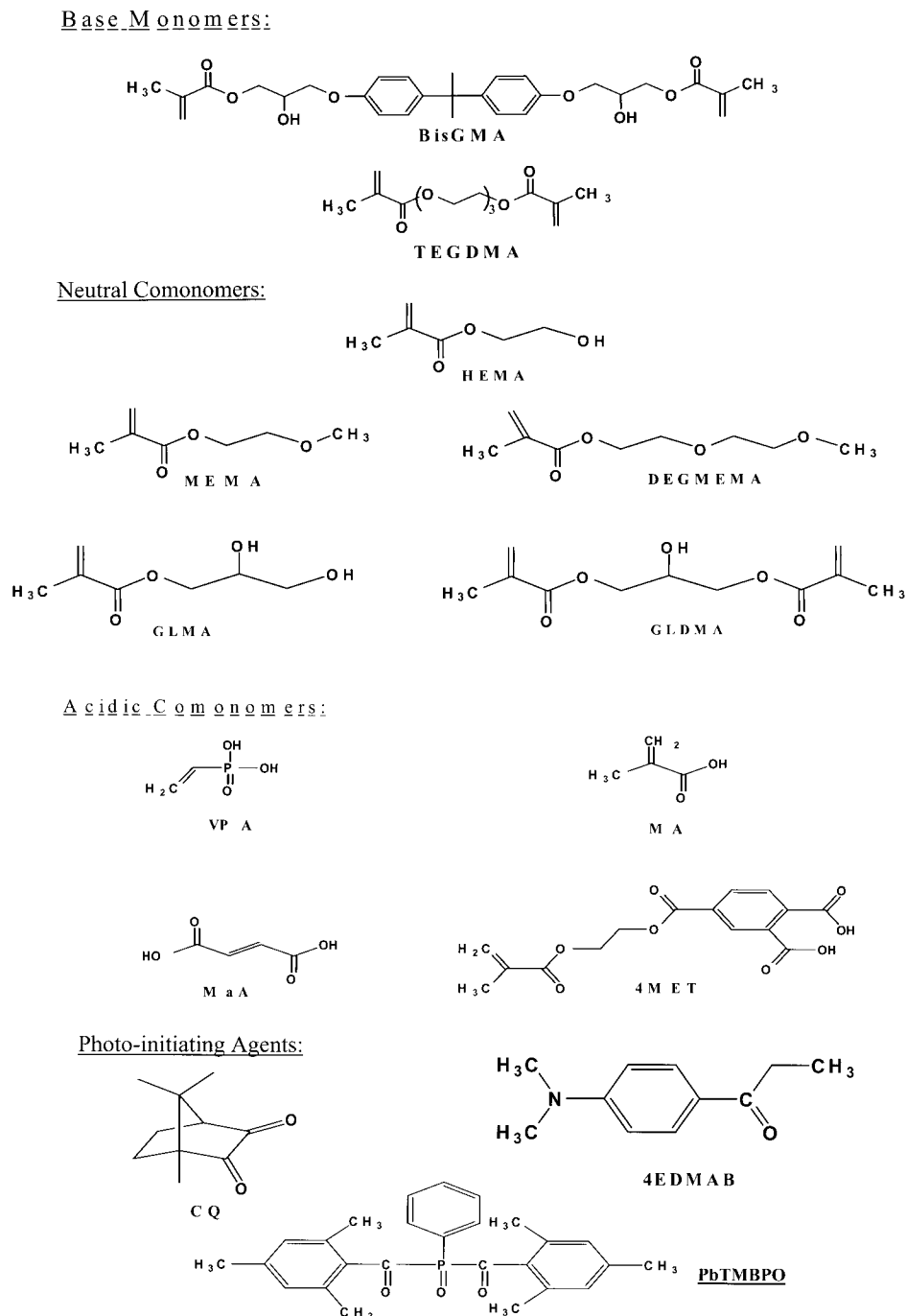


Figure 1. Chemical structure of the monomers and photocuring agents used in the study.

PbTMBPO (BT2) served as control resins. The third component in the neutral monomer series and the acidic monomer series were introduced at mass levels corresponding to either an equivalent molar mass of HEMA or 4MET, respectively. The level of HEMA comonomer chosen corresponds to its concentration in the BTH matrix, which resulted in high bioactivity (ion release) of the corresponding ACP composites.^{5,9,10} The level of 4MET comonomer was determined by its solubility in BT resin. Compositions of the experimental ternary resins and the binary controls are indicated in Table II.

Precipitation and characterization of Zr-ACP filler

Zr-ACP precipitated instantaneously in a closed system at 23°C upon rapidly mixing equal volumes of a 800 mmol/L Ca(NO₃)₂ solution, a 536 mmol/L Na₂HPO₄ solution that contained a molar fraction of 2% Na₄P₂O₇ as a stabilizing component for ACP, and an appropriate volume of a 250 mmol/L ZrOCl₂ solution (mol fraction of 10% ZrOCl₂ based on the Ca reactant). The reaction pH varied between 8.6 and 9.0. The suspension was filtered, the solid phase washed

TABLE II
Composition (Mass Fraction %) of Experimental Resins Evaluated in the Study

a. Bis-GMA/TEGDMA/neutral termonomer series.							
Component/resin	BT1	BTH	BTM	BTD	BTGm	BTGd	
Bis-GMA	49.50	37.00	35.65	31.50	34.00	27.50	
TEGDMA	49.50	37.00	35.65	31.50	34.00	27.50	
HEMA	—	25.00	—	—	—	—	
MEMA	—	—	27.70	—	—	—	
DEGMEMA	—	—	—	36.00	—	—	
GLMA	—	—	—	—	31.00	—	
GLDMA	—	—	—	—	—	44.00	
CQ	0.20	0.20	0.20	0.20	0.20	0.20	
4EDMAB	0.80	0.80	0.80	0.80	0.80	0.80	

b. Bis-GMA/TEGDMA/acidic termonomer series.						
Component/resin	BT2	BTVPA	BTMA	BTMaA	BT4MET	
Bis-GMA	49.03	48.21	48.37	48.37	46.57	
TEGDMA	49.03	48.21	48.37	48.37	46.57	
VPA	—	1.64	—	—	—	
MA	—	—	1.30	—	—	
MaA	—	—	—	1.30	—	
4MET	—	—	—	—	4.90	
PbTMBPO	1.94	1.94	1.96	1.96	1.96	

subsequently with ice-cold ammoniated water, and acetone and then lyophilized. The amorphous state of Zr-ACP was verified by powder X-ray diffraction (XRD: Rigaku X-ray diffractometer, Rigaku/USA Inc., Danvers, MA) and Fourier-transform spectroscopy (FTIR: Nicolet Magna-IR FTIR System 550 spectrophotometer, Nicolet Instrument Corporation, Madison, WI). The standard uncertainty of measuring the *d*-spacing values was 0.0013, and the measured *d*-values were within 0.05% of the reported values of NIST SRM 640 (silicon powder, $2\theta = 28.442$, $d = 3.1355$). The wavelength accuracy of FTIR measurements was $\leq 0.01 \text{ cm}^{-1}$ at 2000 cm^{-1} . Morphological/topological features of the filler, after the specimen was sputter-coated with gold, were examined by scanning electron microscopy (SEM; JSM-5400 instrument JEOL Inc., Peabody, MA). Zr-ACP's particle size distribution (PSD) was determined by gravitational and centrifugal sedimentation analysis (SA-CP3 particle size analyzer, Shimadzu Scientific Instruments, Inc., Columbia, MD) following dispersion of the solid in isopropanol and 10 min ultrasonication. Water content of the filler was determined by thermogravimetric analysis (TGA; PerkinElmer 7 Series Thermal Analysis System, Norwalk, CT). The TGA (three separate runs) were performed by heating 5 to 10 mg of powdered Zr-ACP at the rate of $20^\circ\text{C}/\text{min}$ over a temperature range of 30 to 600°C in air. The surface or loosely bound water was attributed to the mass loss that occurred from 23 to 125°C . Structural or more tightly bound water was attributed to the mass loss that occurred from 150 to 600°C . The Ca/ PO_4 ratio of the solids after dissolution in HCl was calculated from solution Ca^{2+} (atomic adsorption spectroscopy (AAS), PerkinElmer Model 603 spectrophotometer (PerkinElmer, Norwalk, CT) and PO_4 (UV/VIS Carey Model 219 spectrophotometer (Varian Analytical Instruments, Palo Alto, CA) values.

Preparation of composite and unfilled resin (copolymer) specimens

Composite pastes were made from mixing the various resins (Table IIa and b; mass fraction 60%) and the Zr-ACP filler (mass fraction 40%) by hand spatulation. The homogenized pastes were kept under a moderate vacuum (2.7 kPa) overnight to eliminate the air entrained during mixing. The pastes were molded into disks (15.8 to 19.8 mm in diameter and 1.55 to 1.81 mm in thickness) by filling the circular openings of flat Teflon molds, covering each side of the mold with a Mylar film plus a glass slide, and then clamping the assembly together with spring clips. The disks were photopolymerized by irradiating sequentially each face of the mold assembly for 120 s with visible light (Triad 2000, Dentsply International, York, PA). The unfilled resin (copolymer) disk specimens were prepared using circular Teflon molds with one open face that were 14.8 to 15.3 mm in diameter and 0.8 to 1.2 mm in thickness. Thus, the molds for the unfilled resins had a Teflon bottom layer to prevent the resin from seeping out the bottom of the mold. The resin was poured into the cavity, and the filled cavity was then covered with Mylar film and a glass slide. The assembly was not clamped together by spring clips to avoid introducing air voids. The unfilled disks were first photo-polymerized on the glass slide-face of the mold for 120 s, and then the cured disks were removed from their molds and cured on the reverse side for 120 s.

Evaluation of copolymers and composites

To determine the degree of conversion (DC) attained after polymerization of the unfilled resins (copolymers)

and their composites, mid-FTIR spectroscopy was employed. Changes in the 1637 cm^{-1} absorption band for the vinyl group against that of the phenyl ring at 1582 cm^{-1} (used as the internal standard) after photo-curing and storage for 24 h at 23°C were monitored. FTIR spectra were acquired by collecting 64 scans at two wavenumber resolution (relative uncertainty of 0.5 cm^{-1}). At least triplicate measurements were performed for each experimental group.

Biaxial flexure strength (BFS) of the dry and wet (after 2 weeks of immersion in HEPES-buffered, $\text{pH} = 7.40$, saline solutions at 23°C) copolymer and composite disk specimens (three or more specimen per group) were determined by using a computer-controlled Universal Testing Machine (Instron 5500R, Instron Corp., Canton, MA; crosshead speed: 0.5 mm/min) operated by Testworks4 software. The BFS was calculated according to mathematical expressions given in ref. 12.

Statistical data analysis

One standard deviation (SD) is given in this article for comparative purposes as the estimated standard uncertainty of the measurements. These values should not be compared with data obtained in other laboratories under different conditions. Experimental data were analyzed by ANOVA ($\alpha = 0.05$). Significant differences between specific groups were determined by all pairwise multiple comparisons.

RESULTS

The Zr-ACP employed in this study showed no discrete XRD peaks. Its XRD pattern consisted of two diffuse, broad bands characteristic of such commonly recognized noncrystalline substances as glasses and certain polymers [Fig. 2(a)]. A complementary FTIR spectrum of the same filler [Fig. 2(b)] showed only two wide bands in the region of 1200 to 900 cm^{-1} and 630 to 500 cm^{-1} , typical for phosphate stretching and phosphate bending, respectively, of noncrystalline calcium phosphate. The PSD results [Fig. 3(a)] indicated highly heterogeneous, agglomerated particles with sizes (expressed as the equivalent spherical diameter) ranging from submicrometer values up to $80\text{ }\mu\text{m}$. The median diameter (d_m) and the specific surface area (SSA) of the Zr-ACP filler calculated from the three independent PSD measurements were: $d_m = (5.9 \pm 0.7)\text{ }\mu\text{m}$ and $\text{SSA} = (0.53 \pm 0.11)\text{ m}^2/\text{g}$. Heterogeneity of the Zr-ACP's PSD was reflected in the SEM results [Fig. 3(b)]. Total water content of the powder was equal to a mass fraction of 16.6% , of which approximately 72% corresponded to the surface-bound (mobile water) and approximately 28% was probably structurally incorporated. The Ca/PO_4 ratio of the filler was 1.864 ± 0.102 .

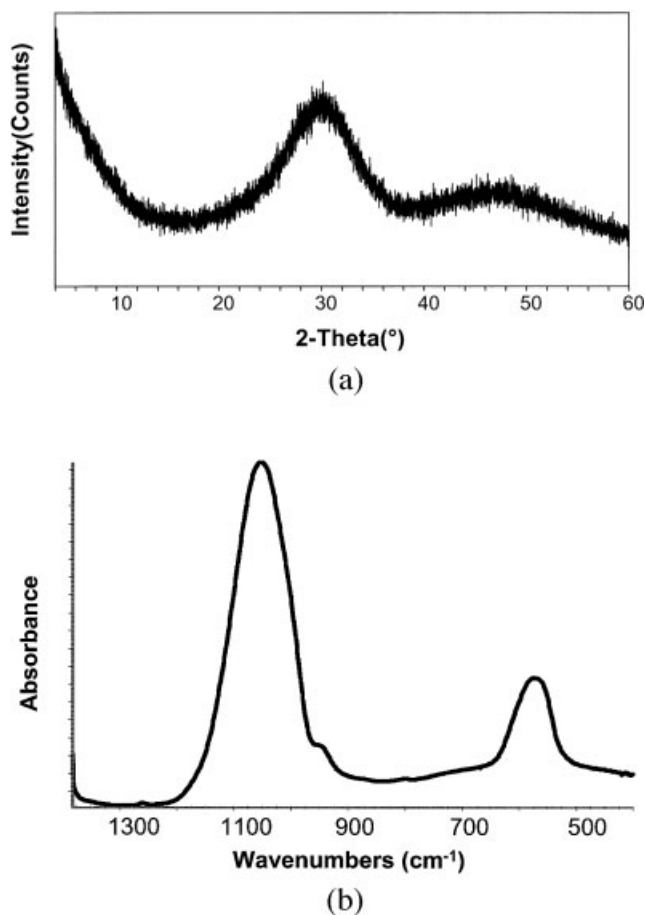


Figure 2. XRD pattern (a) and FTIR spectrum (b) of the Zr-ACP filler utilized in the study.

The results of the BFS testing of dry (before immersion) and wet (after immersion in saline solutions) copolymer and composite specimens are presented in Figure 4 (neutral termonomer series) and Figure 5 (acidic termonomer series). One-way ANOVA of the BFS data revealed that the differences in the mean values among each group (dry copolymers, wet copolymers, dry composites, wet composites) of the neutral termonomer series were significant ($p \leq 0.033$). Similar results were obtained for both dry and wet BT/acidic termonomer composites ($p < 0.001$). However, the mean BFS values of dry and wet copolymers in the acidic termonomer series were not significantly different ($p = 0.104$ and 0.590 , respectively). Additional analysis of the BT/neutral termonomer specimens (all pair-wise multiple comparisons; Tukey test at 95% confidence interval) revealed the following order of decreasing strength for dry copolymer: BT1, BTH, BTM, BTGd; average BFS = $76.6 \pm 12.4\text{ MPa}$ > BTD, BTGm; average BFS = $61.1 \pm 11.3\text{ MPa}$; an average BFS of $71.8 \pm 14.1\text{ MPa}$ for all wet copolymers; an average BFS of $61.9 \pm 9.5\text{ MPa}$ for all dry composites and the following relation for wet composites: BT1; BFS = $52.3 \pm 5.1\text{ MPa}$ > all ternary formulations;

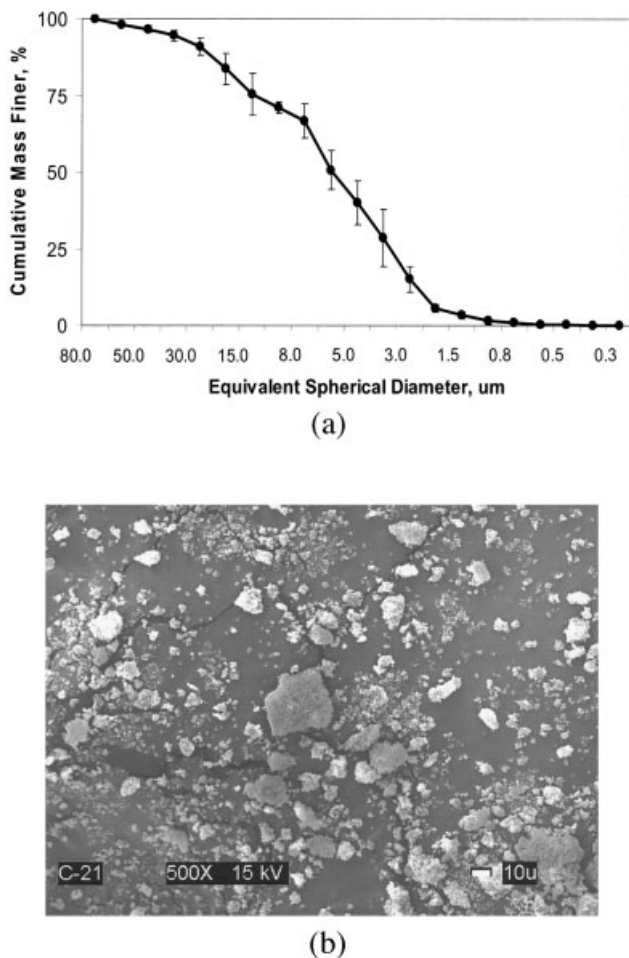


Figure 3. Cumulative particle size distribution (a; mean \pm SD (indicated by bars) and the SEM image of the Zr-ACP powder (b).

average BFS = 29.9 ± 7.9 MPa. The differences in the BFS of dry versus wet BT/neutral termonomer specimens were found (*t*-test, 95% confidence interval, power of 0.800) statistically insignificant for copolymers ($0.080 \leq p \leq 0.909$) and highly significant for composites ($p \leq 0.002$). Comparison of copolymers versus composite specimens showed no difference ($0.079 \leq p \leq 0.668$) for dry samples and significant difference ($p \leq 0.018$) for wet samples.

The average BFS values of the dry and wet copolymers in the BT/acidic termonomer series were 95.0 ± 33.8 MPa and 61.6 ± 28.6 MPa, respectively. The following order of decreasing BFS was established: BTMA, BT4MET; 86.4 ± 13.9 MPa > BT2, BTVPA, BTMaA; 67.9 ± 9.1 MPa for dry composites and BT4MET; 66.5 ± 13.3 MPa > BT2; 48.4 ± 6.7 MPa > BTMA; 37.8 ± 6.4 MPa > BTVPA, BTMaA; 29.1 ± 3.1 MPa for wet composites. The differences in the BFS of dry versus wet BT/acidic termonomer specimens were found (*t*-test) not statistically significant for BT2, BTVPA, and BTMA copolymers ($0.055 \leq p \leq 0.747$), marginally significant for BT4MET copolymers ($p =$

0.046) and highly significant for BTMaA copolymers ($p = 0.005$) and all composites ($p < 0.001$). The BFS of dry copolymer versus dry composite showed no difference ($0.288 \leq p \leq 0.923$) for all but BTMaA specimens ($p < 0.001$). Comparison of wet copolymer versus wet composites specimens revealed more complex behavior; no change in control and BTMaA systems ($0.078 \leq p \leq 0.328$) and significant differences in BTVPA, BTMa, and BT4MET samples ($0.005 \leq p \leq 0.03$). In the case of the BT4MET composites a reverse trend in BFS seems to have occurred in going from dry to wet specimens, although the differences were not statistically significant.

The results of the DC screening of copolymers and Zr-ACP composites in both experimental groups are summarized in Figures 6 and 7. One-way ANOVA of the DC data for both series copolymers and composites revealed that the differences in the mean values among each group were statistically significant ($p < 0.001$). Further data analysis (Tukey test) indicated the following order of the decreasing DC (mean value \pm standard deviation) in the neutral termonomer series: for copolymers—BTD; $87.0 \pm 0.8\%$ > BTH, BTM; $79.7 \pm 1.7\%$ > BT1, BTGm; $73.2 \pm 3.3\%$ > BTGd; $66.5 \pm 1.8\%$, and for composites—BTD; $75.3 \pm 3.0\%$ > BT1, BTH, BTGm; $67.5 \pm 1.5\%$ > BTM, BTGd; $61.3 \pm 3.3\%$. The DC of both copolymers and composites in BT/acidic termonomer series showed practically no dependence on structural variations of the acidic comonomer. It decreased as follows: for copolymers—BT2, BTVPA, BTMA, BT4MET; $73.2 \pm 3.0\%$ > BTMaA 63.5 ± 4.0 , and for composites—BT2, BTMA, BTMaA, BT4MET; $67.4 \pm 2.7\%$ > BVPA $60.6 \pm 4.2\%$. Generally, the DC of composites were lower than the DCs of the corresponding copolymers regardless of the resin matrix composition (the only exception is BTMaA where, surprisingly, the reverse effect was observed).

DISCUSSION

The mechanical strength of both dry and wet copolymers in the BT/neutral termonomer series was unaffected by the structural variations of comonomers. However, introduction of the bioactive ACP filler and exposure of composite specimens to aqueous environment significantly reduced their BFS values. The strength of dry composite specimens decreased on average 15% compared to copolymers, and deteriorated further upon soaking (additional 51% reduction on average). Similar trends were observed in BT/acidic termonomer series. However, in this series, a reduction of almost 35% in the BFS of dry versus wet copolymers occurred but was found statistically insignificant due to the extreme data scattering. The copolymer derived from BTMaA exhibited the greatest vari-

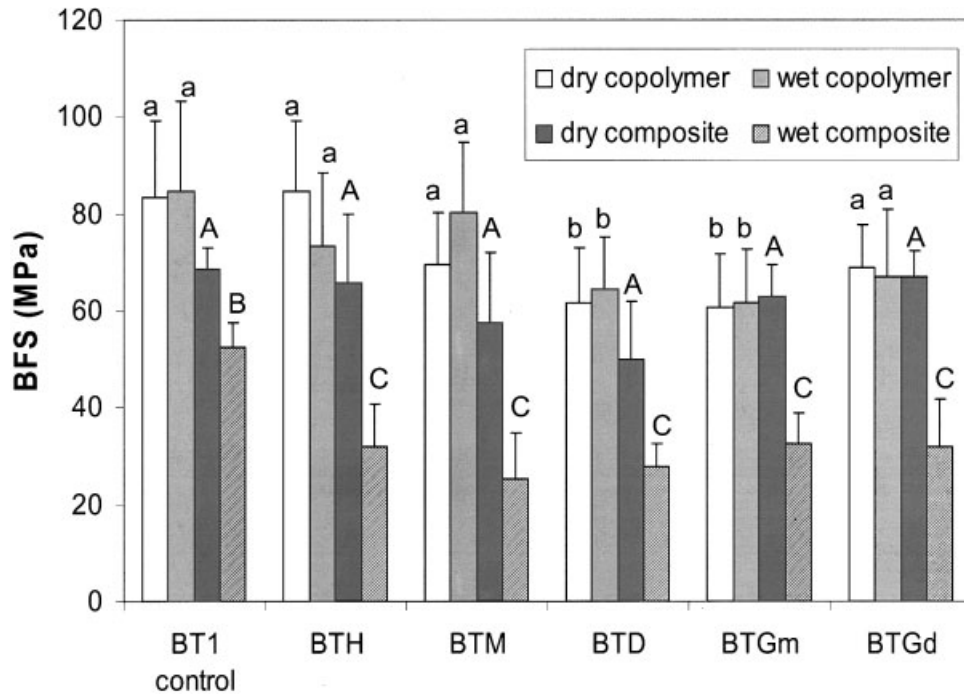


Figure 4. Biaxial flexure strength [BFS; mean + SD (indicated by bars)] of dry and wet BT/neutral termonomer specimens (copolymers and composites). The number of runs in each experimental group $5 \leq n \leq 12$. The different letters (lower case letters for copolymers and upper case letters for composites) indicate significant differences (Tukey test at 95% confidence interval).

ation in strength after aqueous immersion in going from dry to wet state. This severe drop in strength may reflect an increase in hydrophilicity of the copol-

mer due to the presence of two carboxylic acid groups in MaA. The remarkably high BFS of the dry copolymer may be due to the effect of increased

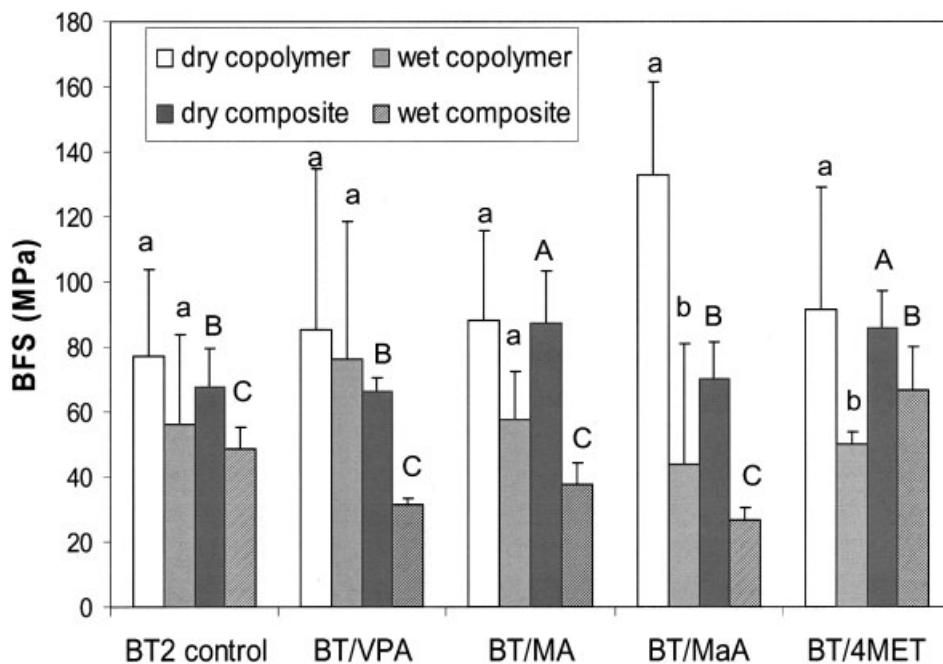


Figure 5. Biaxial flexure strength [BFS; mean + SD (indicated by bars)] of dry and wet BT/acidic termonomer specimens (copolymers and composites). The number of runs in each experimental group $8 \leq n \leq 14$. The different letters (lower case letters for copolymers and upper case letters for composites) indicate significant differences (Tukey test at 95% confidence interval).

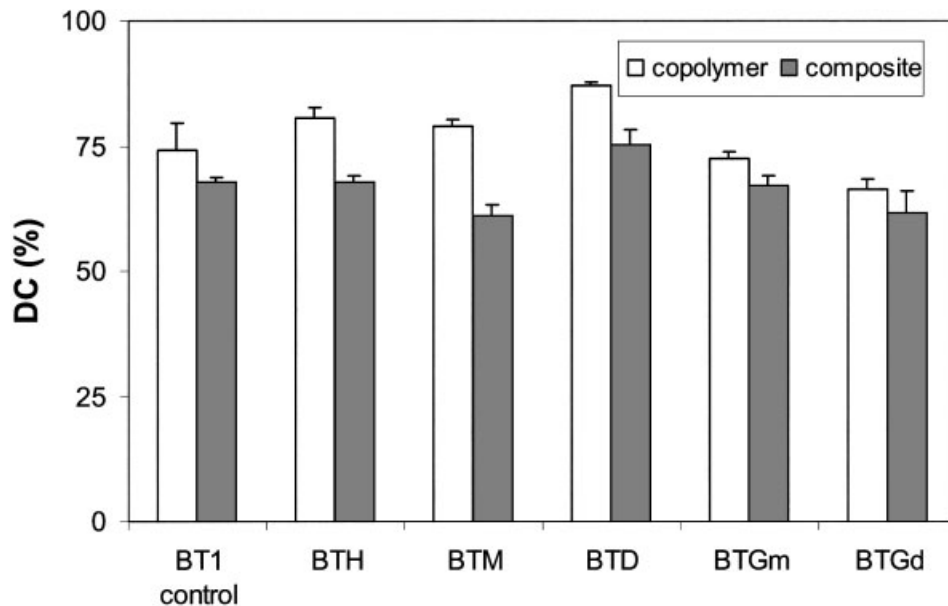


Figure 6. Degree of conversion [DC; mean + SD (indicated by bars)] of BT/neutral termonomer specimens (copolymers and composites) attained 24 h after photocuring. The number of runs in each experimental group $6 \leq n \leq 12$.

crosslinking arising from enhanced intermolecular hydrogen bonding mediated primarily by the favorable arrangement of the two pendant carboxylic acid groups of MaA in the copolymer. Disruption by water of the hydrogen bond-mediated crosslinks may explain the precipitous drop in BFS values.

Dry composite specimens derived from BT/acidic termonomer resins were, on average, 18% weaker than the unfilled dry copolymers. Soaking again had dramatic effect on the BFS; further reduction ranged from moderate (23% for BT4MET composites) to high (52 to 62% for the other acidic composites). This reduction in mechanical strength is caused by either

reduction in ACP's intactness and rigidity at the filler/matrix interface due to the chemical reactions involving ACP and acid groups, spatial changes that may have occurred during the calcium/phosphate ion efflux, internal ACP to Ap conversion, or excessive water absorption. Extensive water sorption/desorption studies need to be performed to determine if there is a positive correlation between the observed strength reduction and polymer matrix plasticization by water.

The extent of DC reduction of unfilled copolymers versus composites observed with acidic, carboxylate-containing comonomers averaged (4.5 to 5.7%, with the exception of VPA where reduction was 16.4%) was

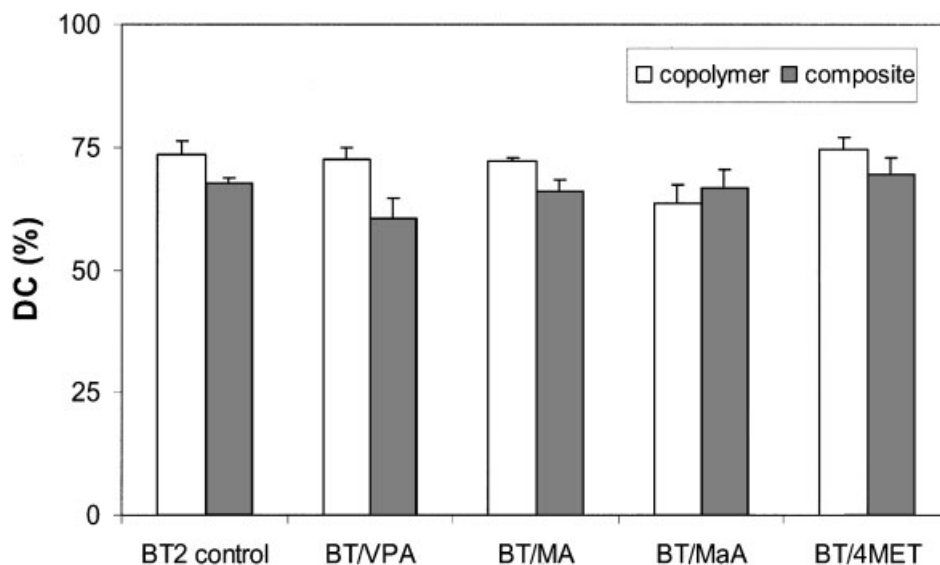


Figure 7. Degree of conversion [DC; mean + SD (indicated by bars)] of BT/acidic termonomer specimens (copolymers and composites) attained 24 h after photocuring. The number of runs in each experimental group $6 \leq n \leq 13$.

lower compared to the neutral comonomers in which the reduction varied from 7.8 to 15.3%. The differential in conversion for copolymer and composite was found to be statistically significant (*t*-test) for all but BT1 and BTGd specimens from the neutral termonomer series and BTMaA and BT4MET specimens from the acidic termonomer series. The monomer system based on DEGMEMA, i.e., the BTD resin, showed the highest DC in both unfilled copolymer and composites, probably because of the highly flexible nature of this monomer. This requires acceptance of the hypothesis that termonomer systems yielded materials with higher DC than a Bis-GMA/TEGDMA binary system. The observed reduction in DC in going from unfilled polymer to ACP composite is most likely due to the reduction in exotherm of resin polymerization by the filler phase. However, other factors such as greater air entrapment and light scattering (facilitated in part by the highly heterogeneous PSD of the ACP) may also contribute to this reduction. The lower extent of DC reduction of unfilled, carboxylate-containing copolymers versus their composites compared to DC reduction of copolymers from the nonacidic termonomer series versus their composites may be explained in part by the much lower molar mass of the acidic comonomers compared to the neutral comonomers. Also, the expected greater affinity of the acidic comonomers for ACP, especially those with carboxylic acid functionalities, may enhance the interfacial conversion of methacrylate groups more so than the neutral termonomer systems.

In conclusion, it seems that varying the Bis-GMA/TEGDMA resin matrix by adding an analog of HEMA may not be sufficient to attain both improved mechanical properties and methacrylate conversion of ACP-filled composites. Of the analogs studied, DEGMEMA gave the highest conversion. Introducing an acidic surface-active comonomer to BisGMA/TEGDMA in some cases improved the strength of dry specimens but not the strength of wet specimens. Significantly, the 4MET comonomer gave enhanced BFS values in both cases. To improve the interfacial state between the ACP filler and the polymer it is essential to achieve uniform distribution of the ACP particulate filler in the polymer matrix and, in turn, minimize the formation of filler-rich and filler-depleted areas within the composites. This is especially important with respect to the performance of composites in aqueous environments since voids or nonbonding spaces at the filler/matrix interface may increase the water sorption of composites.¹³⁻¹⁵ Future studies in our group will focus on minimizing the random ACP clustering within the matrices. More homogeneous particle size distribution of the ACP, and in turn, improved dispersion of the filler in polymer matrices is expected to be achieved via modified synthetic proto-

cols and/or milling procedures. Such fillers will then be formulated with fine-tuned matrix resins to achieve desired physicochemical and mechanical performance. As a result of this study, it would seem that the inclusion of DEGMEMA and 4MET, at optimum levels into the polymer matrices may aid in attaining a high level of DC while also maintaining the mechanical integrity of composites upon aqueous exposure.

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