

Effect of bifunctional comonomers on mechanical strength and water sorption of amorphous calcium phosphate- and silanized glass-filled Bis-GMA-based composites

Drago Skrtic^{a,*}, Joseph M. Antonucci^b

^a American Dental Association Health Foundation, Paffenbarger Research Center, National Institute of Standards and Technology, 100 Bureau Drive Stop 8546, Gaithersburg, MD 20899-8546, USA

^b Polymers Division, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

Received 27 September 2002; accepted 20 February 2003

Abstract

This study seeks to elucidate structure–property relationships in a series of unfilled dental copolymers and their composites. The copolymers/composites were derived from photo-activated binary monomer systems based on 2,2-bis[*p*-2'-hydroxy-3'-methacryloxypropoxy]phenyl] propane (Bis-GMA) and equimolar amounts of a bifunctional, surface-active comonomer, i.e., 2-hydroxyethyl methacrylate (HEMA), glycerol dimethacrylate (GDMA) or ethylene glycol methacrylate phosphate (PHEMA). Triethyleneglycol dimethacrylate, a widely used comonomer for Bis-GMA, was used as a control. Two types of fillers were investigated: (1) a hydrophilic, silica-modified amorphous calcium phosphate (Si-ACP) and (2) a more hydrophobic, silanized nanosized silica (*n*-SiO₂). Both the unfilled copolymers and their composites were evaluated for biaxial flexure strength (BFS), both dry and wet after 30 days immersion in buffered saline, and for water sorption (WS) and their WS kinetic profiles. The Bis-GMA copolymers and composites derived from HEMA and GDMA had BFS and WS values, as well as WS kinetic profiles, similar to the controls. Copolymers and composites based on Bis-GMA/PHEMA had lower BFS and higher WS values. Si-ACP composites had significantly lower BFS values (that were further diminished on soaking) than their copolymers. WS increased as the level of this filler was increased except for Bis-GMA/PHEMA composites. With *n*-SiO₂ as the filler, a more moderate reduction in BFS occurred compared to the unfilled copolymers. By contrast to Si-ACP composites, the WS of all the *n*-SiO₂ composites decreased with increasing filler level. From this study it is evident that both the chemical structure of the polymer matrix and the type of filler system can have significant effects on the strength and water-related properties of dental composites.

© 2003 Elsevier Science Ltd. All rights reserved.

Keywords: Amorphous calcium phosphate; Silanized glass; Methacrylate composites; Biaxial flexure strength; Water sorption

1. Introduction

Amorphous calcium phosphate (ACP) has been identified as a possible precursor in the biological formation of hydroxyapatite (HAP). Of all the biologically important calcium phosphates, ACP, because of its calcium and phosphate stoichiometry and high, sustained release of calcium and phosphate ions in aqueous media, exhibits the most rapid conversion to HAP. Recently, we have developed unique polymeric dental composites [1–3] that utilized these properties of ACP to

remineralize bovine enamel lesions *in vitro* [4]. However, as currently formulated, these bioactive ACP composites have relatively low mechanical strength and adhesiveness to teeth. To improve their mechanical properties while maintaining sustained release of Ca and PO₄ ions, we have so far focused on: (a) synthesizing ACP fillers with structurally incorporated silica and/or zirconia, (b) developing surface-modified hybrid ACP fillers amenable to treatment by silane coupling agents [5–8], and (c) exploring the effects of polymer matrix composition on the mechanical and physico-chemical properties of ACP composites [9–11]. The objective of this research was to assess the effects of several bifunctional comonomers on certain properties of 2,2-bis[*p*-2'-hydroxy-3'-methacryloxypropoxy]phenyl]

*Corresponding author. Tel.: +1-301-975-3541; fax: +301-963-9143.

E-mail address: drago.skrtic@nist.gov (D. Skrtic).

propane (Bis-GMA)-based dental polymers and selected composites derived from these binary monomer systems. For the purpose of this study, a bifunctional monomer is one that has a surface-active functional group in addition to its methacrylate functionality. Thus, triethyleneglycol dimethacrylate (TEGDMA), a diluent comonomer commonly used with Bis-GMA was substituted by the following bifunctional comonomers: 2-hydroxyethyl methacrylate (HEMA), glycerol dimethacrylate (GDMA), and ethylene glycol methacrylate phosphate (PHEMA). Silica-hybridized ACP or silanized microfine glass (n-SiO₂) was introduced into these Bis-GMA-based resins. Biaxial flexure strength (BFS) and water sorption (WS) were determined in order to assess how polymer and composite compositions affect their mechanical properties and stability.

2. Materials and methods

2.1. Resin formulations

The binary monomer systems matrices employed in this study were formulated from the commercially available monomers listed in Table 1, which were used as received. These comonomer formulations (Table 2) were prepared to have molar equivalency and consisted of 1:1.79 M mixtures Bis-GMA:X (X = TEGDMA, HEMA, GDMA or PHEMA). The comonomer mixtures were activated for visible light photo-polymerization by the addition of mass fractions of 0.2% camphorquinone and 0.8% ethyl 4-*N,N*-dimethylaminobenzoate. The chemical structures of the monomers and components of the photo-initiating system are given in Fig. 1.

2.2. ACP filler

Silica-hybridized ACP (Si-ACP) was synthesized employing the preparation protocol of Eanes et al. [12]. It was spontaneously precipitated in a close system (under CO₂-free N₂ in order to minimize CO₂ adsorption) at 22°C by rapidly mixing equal volumes of a 800 mmol/l Ca(NO₃)₂ solution (Ca reactant) and a 536 mmol/l Na₂HPO₄ solution that contained

10.72 mmol/l Na₄P₂O₇ (PO₄ reactant), and an appropriate amount of tetraethoxysilane (TEOS), introduced as a mixture of mass fractions of 10% TEOS, 10% ethanol, 10% tartaric acid and 70% water. This mixture has proven to effectively prevent premature TEOS gelation, to achieve TEOS:Ca(NO₃)₂ molar ratio of 0.1. The PO₄ reactant was brought to pH 12.5 with 1 mol/l NaOH prior to mixing. After stabilization of the reaction pH, the suspension was filtered, and the solid phase washed with ice-cold ammoniated water and lyophilized. After completion of the isolation and drying procedures, the Si-ACP filler, which is hydrophilic, was kept in a desiccator until used for the preparation of composite disk specimens for BFS and WS evaluation.

The amorphous character of Si-ACP was verified by powder X-ray diffractometry (XRD). The XRD profile of the sample was recorded in the 4° to 60° 2θ range with CuKα radiation (λ = 0.154 nm) using a Rigaku X-ray diffractometer (Rigaku Denki Co., Ltd., Danvers, MA, USA) operating at 40 kV and 40 mA. The sample was step scanned in intervals of 0.010° 2θ at a scanning speed of 2000°/min. The local phosphate environment of the solid was evaluated by recording its FTIR spectra (the KBr pellet technique: 2 mg solid per 400 mg KBr; 4000–400 cm⁻¹) using a Nicolet-Magma-IR FTIR System 550 spectrophotometer (Nicolet Instrument Corp., Madison, WI, USA) purged with dry CO₂-free air.

2.3. Glass filler

Commercially available nanosized amorphous SiO₂ (n-SiO₂, with average particle size 0.04 μm; Degussa

Table 2
Composition of the resins employed in the study (mass fraction, %)^a

Component/resin	BT	BH	BG	BP
Bis-GMA	49.5	68.1	55.0	57.1
TEGDMA	49.5	—	—	—
HEMA	—	30.9	—	—
GDMA	—	—	44.0	—
PHEMA	—	—	—	41.9
CQ	0.2	0.2	0.2	0.2
EDMAB	0.8	0.8	0.8	0.8

^a Molar ratio Bis-GMA:comonomer was kept constant 1:1.79. This ratio corresponds to 1:1 mass ratio of Bis-GMA/TEGDMA resins.

Table 1
Names, acronyms and sources of the monomers and components of photo-initiating system employed for resin formulations

Name	Acronym	Manufacturer
2,2-Bis[<i>p</i> -2'-hydroxy-3'-methacryloxypropoxy]phenyl] propane	Bis-GMA	Esstech, Essington, PA, USA
Triethyleneglycol dimethacrylate	TEGDMA	Esstech, Essington, PA, USA
2-Hydroxyethyl methacrylate	HEMA	Esstech, Essington, PA, USA
glycerol dimethacrylate	GDMA	Esstech, Essington, PA, USA
Ethylene glycol methacrylate phosphate	PHEMA	Aldrich Chem. Co., Milwaukee, WI, USA
Camphorquinone	CQ	Aldrich Chem. Co., Milwaukee, WI, USA
Ethyl 4- <i>N,N</i> -dimethylaminobenzoate	EDMAB	Aldrich Chem. Co., Milwaukee, WI, USA

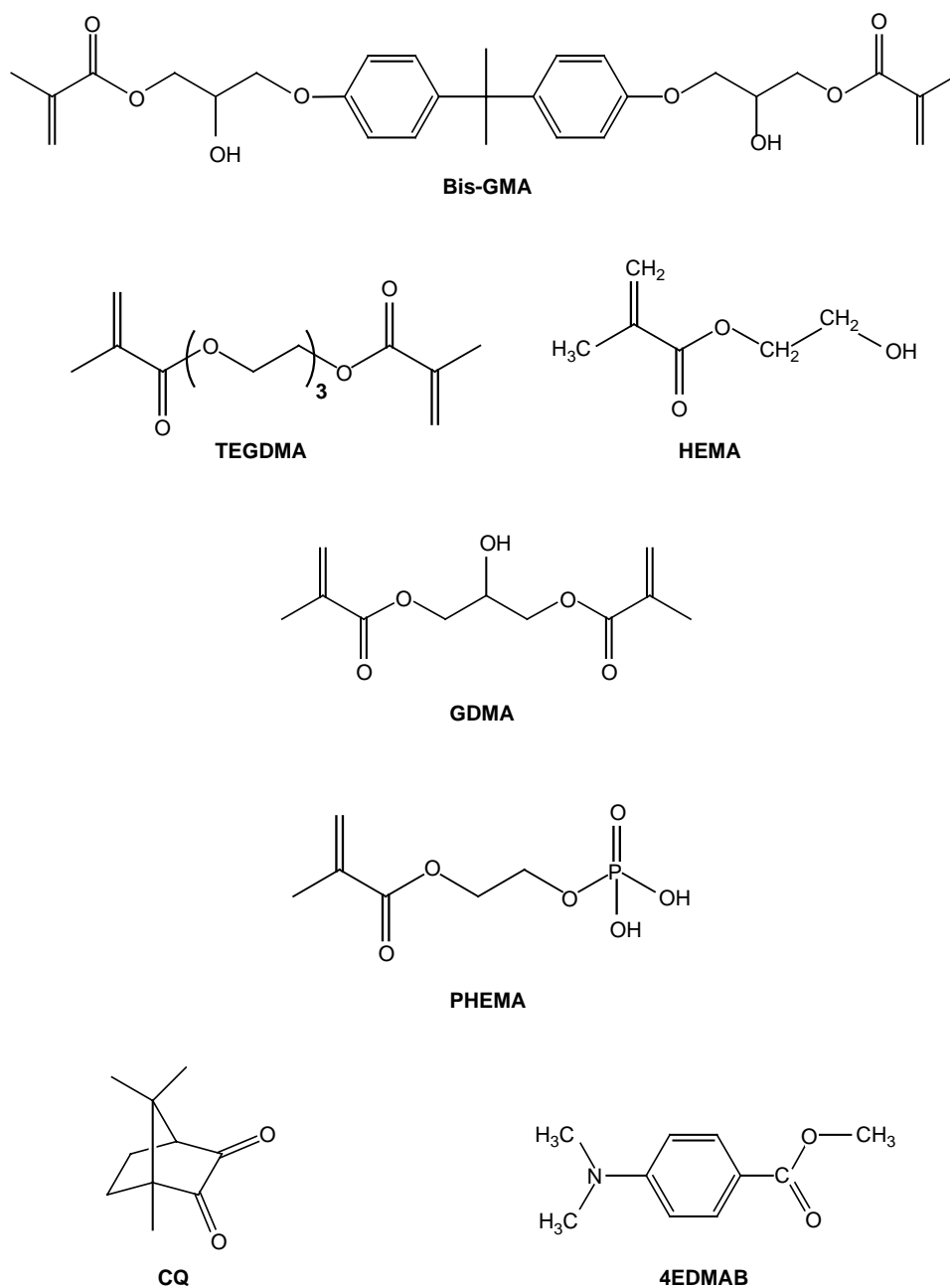


Fig. 1. Chemical structure of the monomers and the components of the photo-initiating system utilized to formulate the resins.

Corporation, Dublin, OH, USA) was silanized with methacryloxypropyl-trimethoxy silane (MPTMS) employing the following protocol: MPTMS (mass fraction of 8.7%) was mixed into a slurry of n-SiO₂ (mass fraction of 89.6%) in cyclohexane containing a mass fraction of 1.7% *n*-propylamine as the silanization catalyst. The silane/n-SiO₂ mixture was rotary evaporated to remove the solvent, *n*-propylamine and volatile byproducts. The silanized glass was then heated at 95°C for 30 min, cooled, washed with cyclohexane to remove unattached MPTMS and other products, and finally, redried under moderate vacuum (2.7 kPa). Compared to

Si-ACP, the silanized n-SiO₂ is quite hydrophobic by contact-angle measurements with water.

2.4. Preparation of composite disk specimens

Composite pastes were formulated from the various monomer systems (Table 2) at mass fraction 75% or 60% by combining them with Si-ACP or silanized n-SiO₂ (mass fraction 25% or 40%) utilizing hand spatulation. The homogenized pastes were kept under vacuum overnight to eliminate the air entrained during mixing. The pastes were then molded to form disks

(15.8–19.8 mm in diameter and 1.55–1.81 mm in height) 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 same procedure was employed to make the disks of unfilled BT, BH, BG and BP monomer mixtures. The disks were photo-polymerized by irradiating each face of the mold assembly for 120 s with visible light (Triad 2000, Dentsply International, York, PA, USA). After postcuring at 37°C in air for 24 h, the disks were randomly selected for the BFS and WS measurements.

2.5. BFS of the composites

Since the measurement of the strength of brittle materials under bi-axial flexure conditions is often considered more reliable than uni-axial flexure (the maximum tensile stresses occur within the central loading area and spurious edge failures are eliminated [13]), a piston-on-three-ball loading arrangement [14], suitable for even slightly warped specimens, was used in this study. The BFS of the dry and wet (after 1 month of immersion in buffered, pH=7.40, NaCl solution at 37°C) composite disk specimens (minimum three replicate disks in each group) was determined by using a computer-controlled universal testing machine (Instron 5500R, Instron Corp., Canton, MA, USA) operated by Instron Merlin Software Series 9. The failure stress was calculated according to the following equation [13,14]:

$$\text{BFS} = AL/t^2, \quad (1)$$

where $A = -[3/4\pi(X - Y)]$, $X = (1 + \nu) \ln(r_1/r_s)^2 + [(1 - \nu)/2](r_1/r_s)^2$, $Y = (1 + \nu)[1 + \ln(r_{sc}/r_s)^2]$, ν is the Poisson's ratio, r_1 is the radius of the piston applying the load at the surface of contact, r_{sc} is the radius of the support circle, r_s is the radius of disk specimen, L is the applied load at failure and t is the thickness of disk specimen.

2.6. Water sorption

A minimum of seven replicate disks in each experimental group were initially dried over anhydrous CaSO₄ until a constant mass was achieved (± 0.1 mg). The specimens were then exposed to an air atmosphere of 75% relative humidity (RH) at room temperature (23°C) by keeping them suspended over a saturated aqueous NaCl slurry in a closed system. Gravimetric mass changes were recorded at 7, 13, 18, 33 and 40 days of exposure to this RH. WS of any individual specimen at any given time interval (t), expressed as a percentage of mass fraction, was calculated using the equation:

$$\text{WS} = [(W_t - W_0)/W_0] \times 100, \quad (2)$$

where W_t represents specimen mass at the time t and W_0 is the mass of a dry specimen (initial mass).

2.7. Statistical analysis

Experimental data were analyzed by multi-factorial ANOVA ($\alpha = 0.05$). To determine significant differences between specific groups, all pairwise multiple comparison procedures were performed.

3. Results

Results of the BFS testing of both dry and wet copolymers as well as the Si-ACP- and n-SiO₂-filled BT, BH, BG and BP composites are summarized in Fig. 2. The following order of decreasing mechanical strength was established for both dry and wet unfilled resins: (BT[(132 ± 27) MPa] = BH[(167 ± 41) MPa] = BG[(155 ± 32) MPa]) > BP[(57 ± 22) MPa]. The apparent decrease in the average BFS of dry vs. wet BT, BH and BG specimens was statistically insignificant ($p > 0.05$; multiple comparisons (Tukey test)), leading to the conclusion that these copolymers were unaffected by soaking. On the contrary, prolonged immersion in buffered saline had a deleterious effect on the BP resins, causing a reduction in the BFS of 88% compared to dry BP specimens.

Introduction of Si-ACP filler into BT, BH and BG copolymers dramatically reduced the BFS of dry specimens. The decrease in the BFS was proportional to the level of Si-ACP: (53–63)% for composites containing a mass fraction of 25% filler, and (68–76)% for composites containing a mass fraction of 40% filler. A similar, although less dramatic, trend was observed with the n-SiO₂: (23–47)% reduction in the BFS for composites containing a mass fraction of 25%, and (43–59)% for composites containing a mass fraction of 40% silanized glass. The strength of dry BP composites compared to the unfilled BP copolymer (its strength was only one-third of the strength of BT, BH and BG copolymers) was reduced (39–56)%, and (12–28)% due to the introduction of Si-ACP and n-SiO₂, respectively. Generally, the strength of Si-ACP-filled BT, BH, BG and BP composites deteriorated upon soaking (only exemption are the BT composites containing a mass fraction of 40% ACP). BT, BH and BG composites containing a mass fraction of 25% n-SiO₂, as well as the BT composites containing a mass fraction of 40% n-SiO₂, were unaffected by soaking. However, at higher loads of n-SiO₂ the strength of BH, BG and BP composites was significantly reduced.

Comparisons of the maximum levels of WS (mass fraction, %) following 40 days exposure to 75% RH for copolymers and Si-ACP- or glass-filled composites are given in Fig. 3. BT, BH and BG copolymers adsorbed a

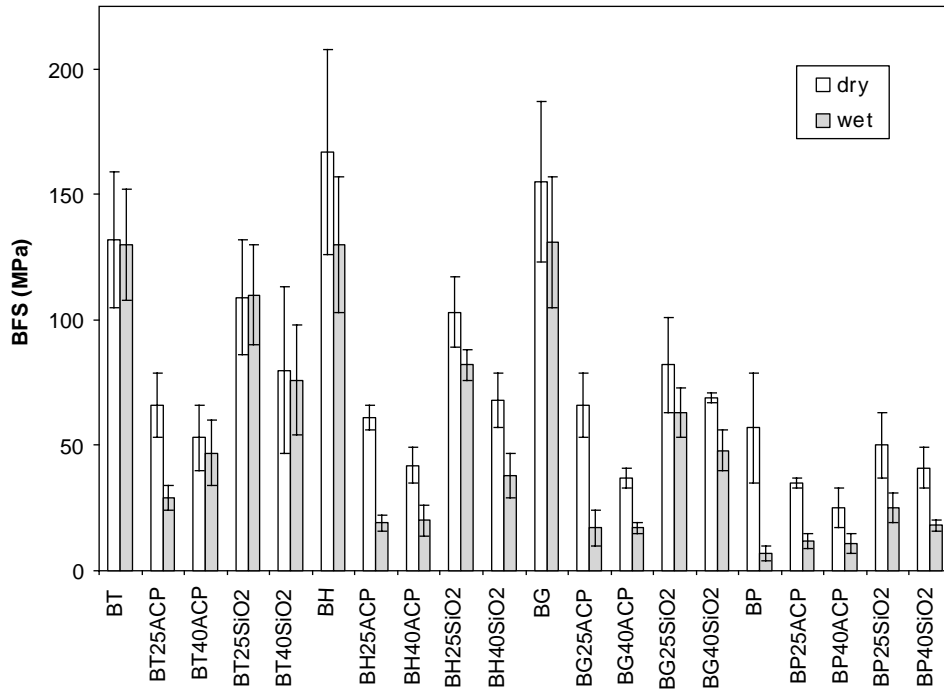


Fig. 2. Comparison of the BFS values (mean \pm SD (indicated by bars)) of dry vs. wet unfilled resins and the ACP- and silanized *n*-SiO₂-filled BT, BH, BG and BP composites containing a mass fraction of 25% or 40% filler. Number of specimens in each experimental group $n \geq 3$.

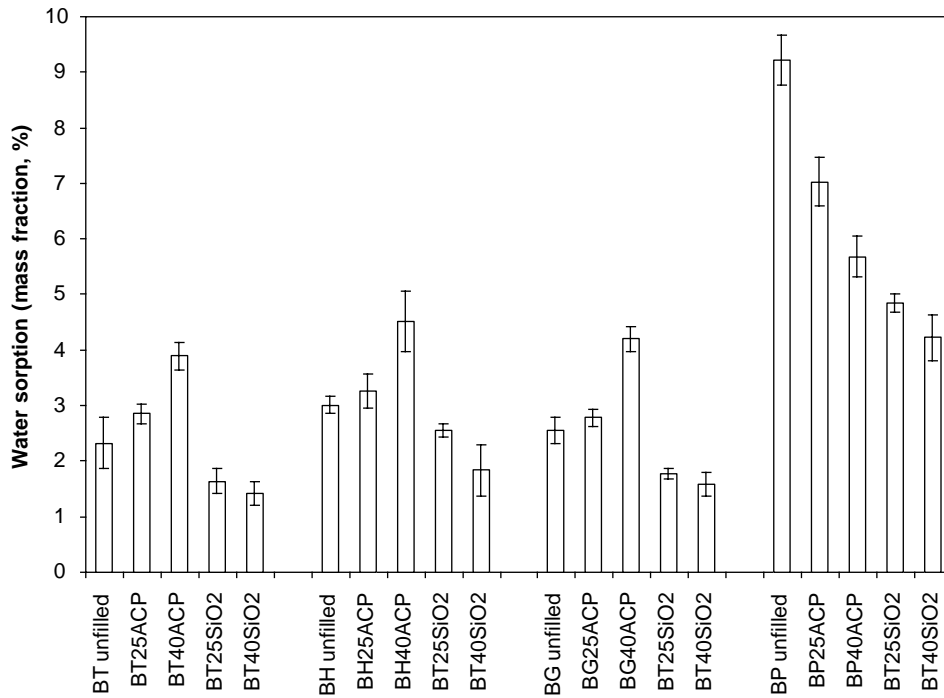


Fig. 3. Maximum WS values (mean \pm SD (indicated by bars)) of unfilled resins and corresponding composites with a mass fraction of 25% or 40% of Si-ACP or silanized *n*-SiO₂ filler after 5 weeks of exposure to 75% RH at 23°C. Number of specimens in each group $n \geq 5$.

maximum of a mass fraction of $(2.32 \pm 0.46)\%$, $(3.01 \pm 0.16)\%$ and $(2.55 \pm 0.24)\%$ water, respectively. The differences in the mean values among the groups are found to be greater than expected by chance ($p < 0.001$; 95% confidence level; one-way ANOVA). Further comparison (Tukey test) revealed that the differences

in WS between the BT and BH copolymers are statistically significant ($p = 0.006$), while the differences between the BT and BG and BH and BG are not ($p = 0.599$ and 0.086 , respectively). In contrast, BP resins adsorbed 3–4 times more water (a mass fraction of $(9.21 \pm 0.45)\%$). The WS of Si-ACP BT, BH and BG

Table 3
The effect of Si-ACP and silanized n-SiO₂ on the WS of resins

Resin/filler	25 ACP ^a	40 ACP	25 SiO ₂	40 SiO ₂
BT	+23 ^b	+56	−29	−39
BH	+8 ^b	+50	−15	−39
BG	+9 ^b	+65	−30	−38
BP	−24	−38	−47	−54

Given numbers represent a relative change (% decrease (−) or % increase (+)) with respect to unfilled resin (number of specimens in each group $n \geq 5$).

^aNumber preceding filler's acronym represents a mass fraction (%) of the filler in the composite.

^bDifferences are statistically insignificant or only marginally significant (Tukey test).

composites showed an apparent increase with the increasing level of Si-ACP in composites compared to unfilled resins. The differences among the groups were again found significant by one-way ANOVA. All pairwise multiple comparisons (Tukey test) revealed significant differences between all but BT25SiO₂ and BT40SiO₂ composites ($p = 0.593$), BH copolymer and BH25ACP composite ($P = 0.785$), BH copolymer and BH25SiO₂ composite ($p = 0.162$), BG copolymer and BG25ACP composite ($p = 0.212$), and BG25SiO₂ and BG40SiO₂ composites ($p = 0.593$). By contrast, introduction of the ACP into BP significantly reduced the BP's resin affinity for WS—the effect being proportional to the amount of ACP filler used. The WS of all n-SiO₂-filled composites significantly decreased with the increasing level of silanized glass compared to unfilled resins. Both differences within (one-way ANOVA; $p < 0.001$) and between the experimental groups (Tukey test, p values < 0.03) were found significant. Changes (%) in the amount of adsorbed water by composites relative to the amounts adsorbed by copolymers are indicated in Table 3.

Besides affecting the final WS, the type of the filler also affected the kinetics of WS (Figs. 4a–d). The initial WS rates were higher for the unfilled and ACP-filled BT, BH and BG composites compared to n-SiO₂-filled ones (Figs. 4a–c). In contrast, the initial WS rates in BP composites (Fig. 4d) were practically independent of the filler type for approximately 2 weeks. Only after that time period the WS rate of ACP-containing BP composites increased relative to n-SiO₂-containing BP composites. Another interesting observation is that only in the BT copolymers and its n-SiO₂ composites, the equilibrium WS value was reached within 18 days, compared to all other systems where it took at least 33 days to reach the steady-state conditions.

4. Discussion

Bis-GMA, a widely used, base monomer for polymeric dental materials has a chemical structure that

includes both hydrophilic and hydrophobic elements. The core diphenylisopropane structure confers on Bis-GMA significant hydrophobicity while the two hydroxyl groups are a major source of the hydrophilicity in the molecule. Overall, however, Bis-GMA is relatively hydrophobic monomer. In addition, diluent monomers such as TEGDMA also exhibits a hydrophilic–hydrophobic nature, but overall is also considered hydrophobic. The majority of commercially available bonding resins contain monomers with both hydrophobic and hydrophilic moieties or hydrophilic monomers such as HEMA [15]. Due to the compositional modifications such resins may have an increased potential to absorb water. Bis-GMA has two OH groups per molecule that can hydrogen bond to adsorbed water. TEGDMA, on the other hand, has three ethylene oxide linkages that can accept hydrogen bonds but not donate them. Substituting HEMA or GDMA for TEGDMA did not affect either the strength of both wet and dry polymerized BH and BG composites. However, a modest but significant increase in WS was observed in BH compared to BT copolymers. Therefore, we conclude that both the BFS and WS of these resins were governed mainly by the ability of Bis-GMA to form hydrogen bonds as both donor and acceptor rather than by the presence of hydrophilic OH functionalities in HEMA or GDMA. Contrary to BH and BG resins, unfilled BP matrices adsorbed more than triple the amounts of water and swelled profoundly upon soaking, resulting in a dramatic reduction of the BFS. The existence of discrete assemblies/sites seen in some polymeric materials based on mixed hydrophilic and hydrophobic components [16] may have caused increased WS in BP matrices. While moderate swelling of the resin may reduce some of the stresses induced by polymerization and may be considered desired when a micro-space exists between the bonding resin and the dentin surface, excessive swelling—as seen with BP formulations—may weaken the bond at the interface [15], and is therefore undesired.

Although WS by dental composite resins is thought to be primarily controlled by the resin matrix [17], the filler in the composite can make a significant contribution to the amount of the water absorbed. As we have shown in this study, it is the type of the filler as well as its loading level that affects both the WS and the BFS of the composites. As seen in Fig. 3, Si-ACP-filled BT, BH and BG composites adsorbed more water than unfilled samples and the sorption effect was proportional to the mass fraction of ACP in the composite. The differences may be explained through increased stresses at the ACP/resin boundaries that in turn promote water diffusion and enhance hydration of ACP surfaces. On the other hand, all composites made with silanized n-SiO₂ filler picked up less water than unfilled BT, BH, BG and BP resins. The WS decreased more as the amount of

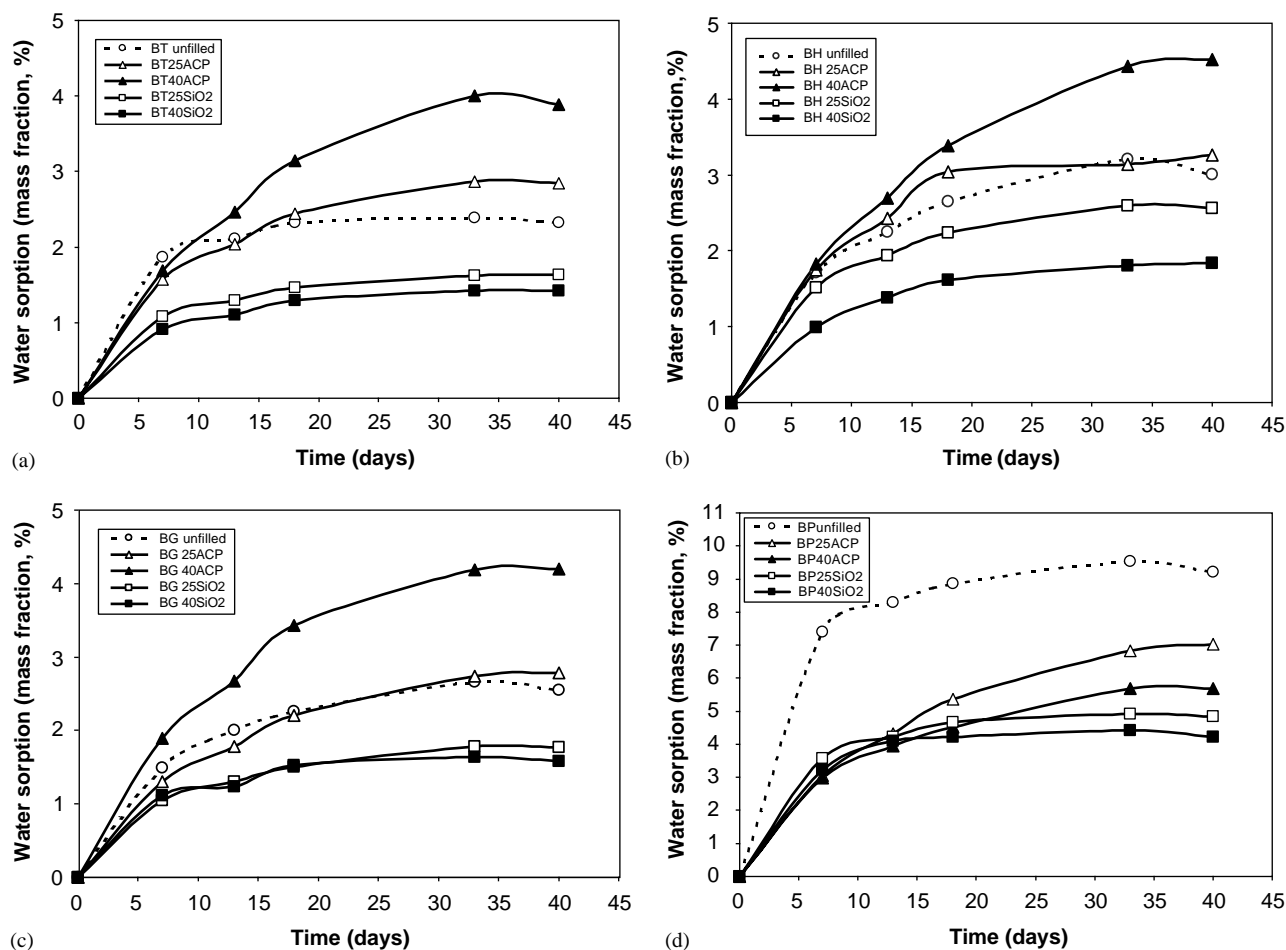


Fig. 4. Kinetic changes in the WS of BT (a), BH (b), BG (c) and BP (d) unfilled resins and ACP or n-SiO₂ composites. Indicated values represent the mean WS for at least five specimens in each group. The SD of indicated values were: mass fraction of <0.26%, <0.32%, <0.19% and <0.37% for BT, BH, BG and BP formulations, respectively.

glass filler in the composites increased. The later results confirm the hypothesis that coupling between the filler and organic matrix (in this study achieved through silanization of glass particles with MPTMS) is another important factor that affects the WS of dental composites. These findings are also consistent with the data showing that, due to the presence of filler particles, the degree of WS of resin-based composites is significantly lower than the WS of bonding resins [18]. However, hybridization of the ACP filler with TEOS seems to be inadequate to achieve the same level of interactions (intermixing/intimate contact) between Si-ACP and the resins.

It has been reported that the WS of the resin restorative materials and bonding resins tends to be less than 1% and less than 4% (mass/mass basis), respectively [15]. Unfilled, ACP filled (mass fraction 25%) as well silanized n-SiO₂-filled (mass fraction 25% and 40%) BT, BH and BG resins fall within the WS range of bonding resins. BT, BH and BG composites containing a mass fraction of 40% Si-ACP, together with unfilled BP resins and BP composites exceed this level.

Several studies [19–21] have addressed the changes in mechanical properties of resin-based composites upon their exposure to water. It was found that prolonged exposure to water of Bis-GMA-based experimental composites [19] affected their fracture toughness, but not elastic modulus, hardness and flexural strength. Our BFS data showed that the type of the filler utilized, rather than resin matrix, determined the strength of the composites both before and after soaking. This finding is in accordance with the results of the mechanical testing of several commercial restorative materials [22], which suggested that fillers themselves, the filler load levels, and the filler–matrix interactions determine the fracture parameters of the composites, rather than the structure of organic matrix. The reduction in the BFS can be correlated with the degree of WS for all ACP-filled BT, BH and BG composites. Higher loads of ACP in these composites resulted in higher WS and lower BFS values. No such correlation could, however, be established for silanized glass-filled BT, BH and BG composites.

In conclusion, the WS and the BFS of Bis-GMA-based composites are affected by the type and the

amount of the filler, in addition to the structural parameters of comonomers. BT resins are proven to be equally promising as BH or BG resins with respect to their affinity to WS and their strength upon soaking. However, PHEMA could potentially be used in Bis-GMA-based resins, but only at significantly reduced levels in order to reduce its deleterious effect on the WS and the BFS.

5. Disclaimer

Certain commercial materials and equipment are identified in this work for adequate definition of the experimental procedures. In no instance does such identification imply recommendation or endorsement by the National Institute of Standards and Technology or the American Dental Association Health Foundation, or that the material and the equipment identified is necessarily the best available for the purpose.

Acknowledgements

This work has been supported by the National Institute of Dental and Craniofacial Research (Grant # DE13169-03), the American Dental Association Health Foundation and the National Institute of Standards and Technology. We are grateful for a gift of Bis-GMA, TEGDMA, HEMA and GDMA from Esstech, Essington, PA, USA.

References

- [1] Antonucci JM, Skrtic D, Eanes ED. Bioactive dental materials based on amorphous calcium phosphate. *Polym Prepr* 1994;35(2):460–1.
- [2] Antonucci JM, Skrtic D, Eanes ED. Remineralizing dental composites based on amorphous calcium phosphate. *Polym Prepr* 1995;36(1):779–80.
- [3] Skrtic D, Eanes ED, Antonucci JM. Polymeric calcium phosphate composites with remineralization potential. In: Gebelein CG, Characher CE, editors. *Industrial biotechnological polymers*. Lancaster: Technomic Publishing Company, 1995. 393pp.
- [4] Skrtic D, Hailer AW, Takagi S, Antonucci JM, Eanes ED. Quantitative assessment of the efficacy of amorphous calcium phosphate/methacrylate composites in remineralizing caries-like lesions artificially produced in bovine enamel. *J Dent Res* 1996;75(9):1679–86.
- [5] Antonucci JM, Skrtic D, Eanes ED. Bioactive polymeric composites based on hybrid amorphous calcium phosphate. *Polym Prepr* 1998;39(2):236–7.
- [6] Antonucci JM, Skrtic D, Hailer AW, Eanes ED. Bioactive polymeric composites based on hybrid amorphous calcium phosphate. In: Ottenbrite RM, Kim SW, editors. *Polymeric drugs and drug delivery systems*, Lancaster: Technomic Publishing Company, 2000. 301pp.
- [7] Skrtic D, Antonucci JM, Eanes ED, Eichmiller FC, Schumacher GE. Physicochemical evaluation of bioactive polymeric composites based on hybrid amorphous calcium phosphates. *J Biomed Mater Res (Appl Biomater)* 2000;53:381–91.
- [8] Antonucci JM, Skrtic D, Eanes ED. Bioactive dental materials based on amorphous calcium phosphate—effect of coupling agents. In: Ottenbrite RM, Huang S, Park K, editors. *Hydrogels and biodegradable polymers for bioapplications*. Washington DC: American Chemical Society, 1996. 243pp.
- [9] Skrtic D, Antonucci JM, Eanes ED. Improved properties of amorphous calcium phosphate fillers in remineralizing resin composites. *Dent Mater* 1996;12:295–301.
- [10] Skrtic D, Antonucci JM, Eanes ED. Polymer matrix effects on the properties of amorphous calcium phosphate-filled composites. *Polym Prepr* 2000;41(2):1705–6.
- [11] Skrtic D, Antonucci JM, Eanes ED. Effect of the monomer and filler system on the remineralizing potential of bioactive dental composites based on amorphous calcium phosphate. *Polym Adv Technol* 2001;12:1–11.
- [12] Eanes ED, Gillessen IH, Posner AS. Intermediate states in the precipitation of hydroxyapatite. *Nature* 1965;208:365–7.
- [13] Ban S, Anusavice KJ. Influence of test method on failure stress of brittle dental materials. *J Dent Res* 1990;69(12):1791–9.
- [14] Kirsten AF, Woley RM. Symmetrical bending of thin circular elastic plates on equally spaced point supports. *J Res Natl Bur Stand* 1967;71C:1–10.
- [15] Burrow MF, Inokoshi S, Tagami J. Water sorption of several bonding resins. *Am J Dent* 1999;12(6):295–8.
- [16] Akashi A, Matsuya Y, Unemori M, Akamine A. The relationship between water absorption characteristics and the mechanical strength of resin-modified glass-ionomer cements in long-term water storage. *Biomaterials* 1999;20:1573–8.
- [17] Venz S, Dickens B. NIR-spectroscopic investigation of water sorption characteristics of dental resins and composites. *J Biomed Mater Res* 1991;25:1231–48.
- [18] Pagniano RP, Johnston WM. Three-year effect of unfilled resin dilution on water sorption of a light-cured microfill and hybrid composite resin. *J Prosthet Dent* 1996;75:364–6.
- [19] Ferracane JL, Berge HX, Condon JR. In vitro aging of dental composites in water. Effect of degree of conversion, filler volume and filler matrix coupling. *J Biomed Mater Res* 1998;42:465–72.
- [20] Feilzer AJ, deGee AJ, Davidson CL. Relaxation of polymerization contraction shear stress by hygroscopic expansion. *J Dent Res* 1991;69:36–9.
- [21] Sarrett DC, Ray S. The effect of water on polymer matrix and composite wear. *Dent Mater* 1994;10:5–10.
- [22] Manhart J, Kunzelmann KH, Chen HY, Hickel R. Mechanical properties of new composite restorative materials. *J Biomed Mater Res (Appl Biomater)* 2000;53:353–61.