

Volumetric contraction and methacrylate conversion in photo-polymerized amorphous calcium phosphate/methacrylate composites

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Abstract

Because of its relatively high solubility in aqueous media and its rapid transformation to hydroxyapatite, amorphous calcium phosphate (ACP) has been utilized as the filler phase of resin-based bioactive composites that have remineralization potential. The objectives of this study were to determine how various methacrylate resins and various types of ACP fillers affect acrylic vinyl conversion and polymerization shrinkage (PS). Several types of photo-crosslinkable resin systems were prepared and admixed with a mass fraction of 40% of either unhybridized, silica- or zirconia-hybridized ACP. After visible light-activated photo-polymerization ACP composites were assessed by near infrared spectroscopy for degree of vinyl conversion and by mercury dilatometry for PS. It was found for these composites that vinyl conversion was independent of filler type but strongly dependent on the type and composition of the resin phase. PS, on the other hand, showed more complex dependence both on the resin type and composition and, in some cases, on the type of ACP. In order to obtain ACP/methacrylate-based composites with maximal vinyl conversion, resin type and composition are of primary importance. However, in order to minimize volume contraction on polymerization it appears necessary to consider both the resin and filler type of these bioactive composites.

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Keywords: Amorphous calcium phosphate; Methacrylate composites; Degree of conversion; Polymerization shrinkage

1. Introduction

Recent research in this laboratory has led to the development of unique, experimental bioactive composites based on polymer matrix phases derived from the ambient polymerization of dental acrylic monomer systems containing amorphous calcium phosphate (ACP) as the filler phase [1,2]. It was also found that when ACP was stabilized by pyrophosphate ($P_2O_7^{4-}$) its intracomposite conversion to hydroxyapatite was retarded. Significantly, it was possible to take advantage of the relatively high solubility of ACP and obtain substantial release of Ca^{2+} and PO_4 ions from such composites. Moreover, the ion levels attained in solution from these releases from composite sealants were

sustainable, and were shown to promote recovery of mineral-deficient tooth structures in vitro [3]. As previously prepared ACP exists as particulate filler with a wide range of sizes and with a propensity towards aggregation. In addition, ACP does not act as reinforcing filler for the polymer matrix phase of these composites. In order to make ACP more interactive with polymeric matrices, tetraethoxysilane (TEOS) and zirconyl chloride ($ZrOCl_2$) have been evaluated as potential hybridizing agents for ACP during its preparation with encouraging results [4].

We have already reported [5] that variations in methacrylate resin chemical structure and composition may affect the rate and extent of ion release from ACP-filled composites, the internal conversion of ACP into HAP, and their mechanical properties. Previous studies of ACP composites primarily utilized the base monomer 2,2-bis[*p*-(2'-hydroxy-3'-methacryloxypropoxy)phenyl]propane (Bis-GMA), the diluent comonomer triethylene glycol dimethacrylate (TEGDMA), the hydrophilic comonomer 2-hydroxyethyl methacrylate (HEMA),

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and the coupling/dispersing agent zirconyl methacrylate (ZrMA) [BTHZ resin]. Although widely utilized in dental composites, most Bis-GMA resin systems have shortcomings such as high polymerization shrinkage (PS) and relatively low cure efficiency at ambient temperatures. These shortcomings can affect the adaptation to tooth structure, physicochemical and mechanical properties and ultimately the service life of Bis-GMA-based composites. Generally, conventional diluent monomers (such as TEGDMA) are used with the highly viscous Bis-GMA in order to obtain resins with tractable viscosities and improved degrees of vinyl conversion (DC). However, their use also augments the degree of PS and the attendant problems of internal strains, gap formation and micro-leakage. The hydroxyl groups of Bis-GMA and the ethylene oxide segments of TEGDMA also contribute to the relatively high water sorption of the resulting copolymers. High concentrations of the structurally more rigid Bis-GMA typically result in monomer systems with relatively low DC and PS [6]. As expected increasing the amount of diluent monomer such as TEGDMA will increase not only DC but also PS. In composites both DC and PS are also affected by the presence of the filler phase.

The objectives of this study were to assess the effects of several photo-curable resin systems and three types of ACP filler phases, combined at the same mass levels, on the vinyl conversion and volume contraction of the resulting composites.

2. Materials and methods

2.1. Methacrylate resin formulations

The photo-activated resins were formulated from the commercial monomers and the photo-initiator components listed in Table 1. The mass fraction composition of each resin is given in Table 2.

2.2. Synthesis and characterization of ACP fillers

u-ACP [7] was prepared by rapidly adding, while stirring, an equal volume of an 800 mmol/l $\text{Ca}(\text{NO}_3)_2$ solution to a 525 mmol/l $\text{Na}_2\text{HPO}_4/11$ mmol/l $\text{Na}_4\text{P}_2\text{O}_7$ solution previously adjusted to pH = 12.5 with 1 mol/l NaOH. The instantaneous precipitation reaction was carried out in a closed system under CO_2 -free N_2 at 22°C. In this way CO_2 adsorption by the precipitate was

Table 1
Monomers and components of photo-initiator system utilized in resin formulations

Component	Acronym	Manufacturer
2,2-Bis[p-(2'-hydroxy-3'-methacryloxypropoxy)phenyl]-propane	Bis-GMA	Esstech, Essington, PA
Triethyleneglycol dimethacrylate	TEGDMA	Esstech, Essington, PA
Pyromellitic glycerol dimethacrylate	PMGDMA	Esstech, Essington, PA
2-Hydroxyethyl methacrylate	HEMA	Esstech, Essington, PA
1,6-Bis(methacryloxy-2-ethoxycarbonylamino)-2,4,4-trimethylhexane	UDMA	Esstech, Essington, PA
Zirconyl dimethacrylate	ZrDMA	Rohm Tech. Inc., Malden, MA
Camphorquinone	CQ	Aldrich Chem. Co., Milwaukee, WI
Ethyl 4- <i>N,N</i> -dimethylaminobenzoate	EDMAB	Aldrich Chem. Co., Milwaukee, WI
2-Benzyl-2-(dimethylamino)-1-(4-(4-morpholinyl)phenyl)-1-butanone	IRGACURE [®] 369	Ciba, Hawthorne, NY
2-Hydroxy-2-methyl-1-phenyl-1-propanone and diphenyl (2,4,6-trimethylbenzoyl) phosphine oxide	DAROCUR [®] 4265	Ciba, Hawthorne, NY

Table 2
Resin compositions (mass fraction; %) used in the preparation of experimental composite specimens

Resin/component	BTHZ	TP	U	U66H	U132H
Bis-GMA	35.50	—	—	—	—
TEGDMA	35.50	48.65	—	—	—
HEMA	27.20	—	—	6.60	13.20
PMGDMA	—	48.65	—	—	—
UDMA	—	—	99.00	92.40	85.80
ZrDMA	0.80	—	—	—	—
CQ	0.20	0.40	0.20	0.20	0.20
EDMAB	0.80	—	0.80	0.80	0.80
IRGACURE [®] 369	—	0.80	—	—	—
DAROCUR [®] 4265	—	1.50	—	—	—

minimized. After the pH stabilized at 10.5–11.0, which took less than 5 min, the suspension was filtered and the solid phase washed with ice-chilled ammoniated water, freeze-dried and lyophilized. Si- and Zr-ACP fillers were prepared by simultaneously adding appropriate volumes of either a previously prepared TEOS solution (mass fraction of 10% TEOS, 10% ethanol, 10% tartaric acid and 70% water) or 0.25 mol/l ZrOCl_2 solution and $\text{Ca}(\text{NO}_3)_2$ solution to the Na_2HPO_4 solution. The composition of the TEOS solution was designed to prevent premature gelation of TEOS. Amounts of hybridizing agent solutions were adjusted to achieve molar ratios of $\text{ZrOCl}_2:\text{Na}_2\text{HPO}_4$ and $\text{TEOS}:\text{Na}_2\text{HPO}_4$ equal to 0.1. The reaction pH was stabilized between 8.6 and 9.3. The suspensions were filtered, and the solid phase washed with ice-cold ammoniated water, freeze-dried and lyophilized.

The amorphous state of lyophilized solids was verified by powder X-ray diffractometry (XRD) and Fourier-transform infrared spectroscopy (FTIR). The XRD profiles of the powdered samples were recorded in the $4\text{--}60^\circ 2\theta$ range with $\text{CuK}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) using a Rigaku X-ray diffractometer (Rigaku/USA Inc., Danvers, MA, USA) operating at 40 kV and 40 mA. The samples were step-scanned in intervals of $0.010^\circ 2\theta$ at a scanning speed of $1.000^\circ/\text{min}$.

The FTIR spectra ($4000\text{--}400 \text{ cm}^{-1}$) of the fillers in KBr pellets were recorded using a Nicolet Magna-IR FTIR System 550 spectrophotometer (Nicolet Instrument Corporation, Madison, WI, USA) purged with dry CO_2 -free air. Specimen pellets were made from approximately 2 mg of the solid and 400 mg of KBr.

2.3. Volumetric contraction of composites

Composite pastes were prepared from the various resins (Table 2; mass fraction 60%) and ACP fillers (mass fraction 40%) by hand spatulation. The homogenized pastes were then kept under a moderate vacuum (2.7 kPa) overnight to eliminate the air entrained during mixing. Volumetric polymerization contraction of the composite resins samples was measured by a computer-controlled mercury dilatometer (ADA Health Foundation, Gaithersburg, MD, USA [8]). A schematic diagram of the dilatometer is given in Fig. 1. The composite paste (58–92 mg) was placed on a 1 mm thick glass plate and positioned so that it is centered inside the large end of a socket member of a glass joint. To make a seal tight, the glass plate was pressed against the socket rim by a clamp. The socket and the attached glass tube were then filled with mercury until it completely covered the specimen and partially filled the tube. A plunger connected to a linear variable displacement transducer (LVDT) was lowered to float on the mercury meniscus. Once the temperature and the height of the mercury column reached steady-state conditions (as determined

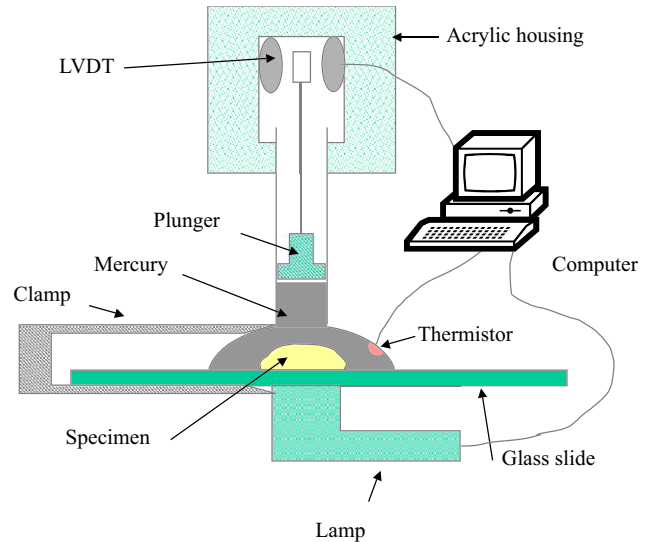


Fig. 1. Schematic diagram of a computer-controlled mercury dilatometer.

via the thermistor and via the LVDT and recorded by a microcomputer), the curing light (Max Lite; Caulk/Dentsply, Milford, DE, USA) was triggered automatically for 60 s and the LVDT and the thermistor readings recorded for 60 min. The curing light was then triggered again for 30 s and data acquisition continued for additional 30 min. If additional shrinkage is observed after the second firing of the lamp, the initial light-curing for 60 s was insufficient to ensure complete consumption of the photo-initiator. Volumetric shrinkage of a specimen corrected for temperature fluctuations during the measurement is plotted as a function of time. The overall shrinkage due to polymerization (volume fraction, %) is calculated based on the known mass of the polymer sample and its density. Sample density is determined by means of Archimedeian principle using an attachment to a microbalance (Sartorius YDK01 Density Determination Kit; Sartorius AG, Goettingen, Germany).

2.4. Methacrylate conversion attained upon polymerization of composites

A non-destructive near infrared (NIR) spectroscopic technique for measuring the methacrylate conversion in dental resins recently developed by Stansbury and Dickens [9] was utilized for this part of the study. This method offers several advantages compared with standard mid-IR analytical procedures: convenient specimen preparation, clinically relevant sample dimensions and non-destructibility (the same specimen can be used in other studies, e.g. water sorption). The NIR spectra (64 co-added scans at four wave-number resolution) were obtained with a Nicolet Magna 550 spectrophotometer (Nicolet Instrument Corporation, Madison, WI, USA) configured with a white light source, a CaF_2 beam splitter and an InSb detector.

To collect spectrum for uncured unfilled resin, a Teflon mold (4.92–5.12 mm in diameter and 2.97–3.31 mm in thickness) was put on a bottom glass slide, filled with resin, covered with a top glass slide, avoiding entrapment of bubbles, and the assembly positioned in a standard FTIR sample holder with a masked 5 mm diameter opening. Immediately after collecting the uncured resin NIR spectrum, each face of the assembly was irradiated for 120 s with visible light (Triad 2000, Dentsply International, York, PA, USA). NIR spectrum of cured resin was collected after a post-cure interval of 24 h. Clamped specimen assemblies were stored in the dark at 37°C during the post-cure period. Following the collection of the NIR spectra, the cured resin samples were disassembled, removed from the molds and their thickness measured by micrometer (standard uncertainty of 0.3 μm).

To collect spectra of uncured composites, their pastes (prepared as described above) were molded in 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 and covering each side of the mold with a glass slide. The assembly was positioned in a standard FTIR sample holder and NIR spectrum of the uncured paste collected. The sample was then photo-polymerized, post-cured, the NIR spectrum of cured composite was acquired, and the thickness of the sample measured (as described above).

Of the two methacrylate=CH₂ NIR absorption bands (4743 cm⁻¹ in the combination region and 6165 cm⁻¹ in the overtone region) the 6165 cm⁻¹ band has a favorable near baseline resolution which facilitates reliable baseline measurements. Therefore, this band was used to assess the methacrylate conversion in paired monomer and polymer spectra of individual samples. Use of an internal reference was not required, provided that the monomer/polymer thickness has been measured [9]. DC was calculated from the decrease in integrated peak area/sample thickness values using the following expression:

$$DC = 100 \left\{ 1 - \frac{(\text{area}/\text{thickness})_{\text{polymer}}}{(\text{area}/\text{thickness})_{\text{monomer}}} \right\}. \quad (1)$$

2.5. Statistical analysis

Experimental data were analyzed by multi-factorial ANOVA ($\alpha = 0.05$). To determine significant differences between specific groups, all pair-wise multiple comparison procedures (two sample *t*-test assuming unequal variances; confidence interval 95%) were performed.

3. Results

An example of a typical PS kinetic curve is given in Fig. 2. Results of dilatometric measurements are

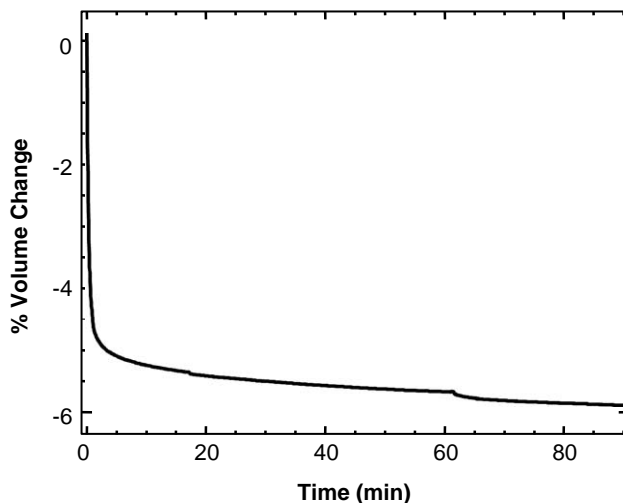


Fig. 2. A typical volumetric contraction—time curve obtained upon light-polymerization of Zr-ACP/TP composite.

summarized in Fig. 3. The PS of u-ACP based BTHZ and TP composites were not significantly different from the PS of Si-ACP or Zr-ACP based BTHZ and TP composites (one-way ANOVA: $p = 0.75$ and 0.13 for BTHZ and TP composites, respectively). On the other hand, the differences in the PS of u-ACP versus Si- and Zr-ACP based UDMA composites ranged from marginally significant (U composites; $p = 0.05$), significant (U66H composites; $p = 0.01$), to very significant (U132H composites; $p = 0.003$). Based on the multiple comparisons of the PS data the following order of decreasing PS as a function of the resin composition was established: BTHZ > TP > [U, U66H, U132H], for u-ACP; [BTHZ, U66H, U132H] > [TP, U] for Si-ACP; and [BTHZ, U66H, U132H] > TP > U, for Zr-ACP.

The NIR conversion results are presented in Fig. 4. The differences between the unfilled resins and the various composites (u-ACP, Si-ACP and Zr-ACP) were found to be very significant (one-way ANOVA) for the BTHZ, TP, U and U66H resins and composites (p values ≤ 0.05) but non-significant for U132H resins and composites. Additional analysis (all pair-wise multiple comparisons) revealed the following order of descending DC: [BTHZ, U132H, U66H] > U \gg TP for unfilled and Si-ACP-filled composites, [BTHZ, U132H] > [U66H, U] \gg TP for u-ACP-filled composites, and BTHZ > [U132H, U66H] > U \gg TP for Zr-ACP-filled composites.

4. Discussion

Ideally, resin systems used in composites should achieve upon polymerization the contradictory goals of both high vinyl conversion and minimal volumetric contraction. A high DC, with homogeneous network formation, is desirable because it maximizes the

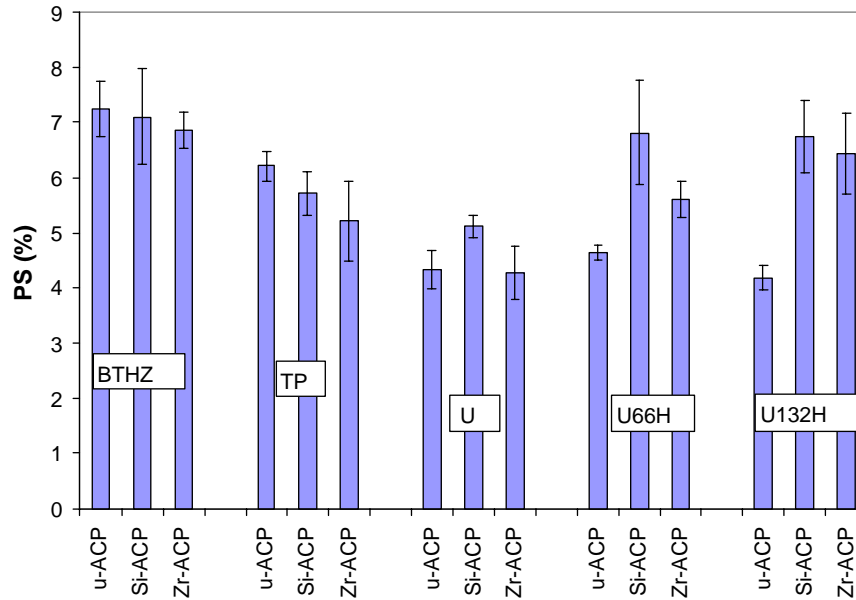


Fig. 3. PS (mean \pm SD (indicated by bars)) of BTHZ, TP, U, U66H and U132H resins filled with u-ACP, Si-ACP or Zr-ACP. Number of samples in each group: $10 \geq n > 3$. The SD is taken as a measure of the standard uncertainty.

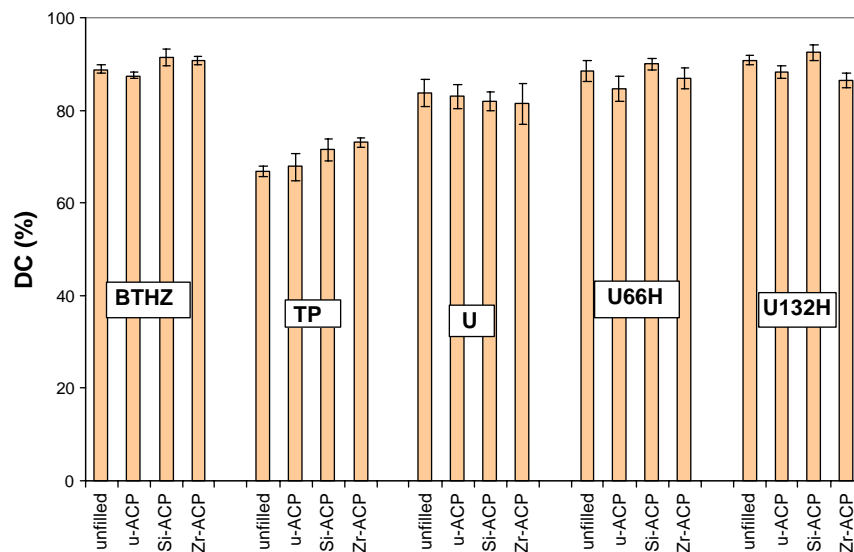


Fig. 4. Degree of methacrylate conversion (DC; mean \pm SD (indicated by bars)) of unfilled, u-ACP-, Si-ACP- and Zr-ACP-filled BTHZ, TP, U, U66H and U132H resins attained at 24h after photo-curing. Number of samples in each group: $10 \geq n > 3$. The SD is taken as a measure of the standard uncertainty.

glass transition temperature of the matrix; thereby rendering it less susceptible to the softening effects of the aqueous oral environment, primarily by plasticization of the matrix but also by degradative attack on all phases of the composite. Since, however, PS is directly correlated with conversion [10,11], a high DC can have undesirable consequences, such as the formation of gaps and stress sites in the microstructure of the composite and at the composite/tooth interface. On the other hand, for a given composite, reduction in DC will lead to lower shrinkage and lower contraction stress [12]. The latter situation also is considered undesirable because of potential for

leachables and reduction in the strength and modulus of the composite.

Especially in the case of bioactive ACP-composites, the level of conversion of methacrylate double bonds attained during polymerization often can be used to indirectly assess the potential leachability of unreacted monomeric and related species, and in turn the relative biocompatibility of the composites. Under given experimental conditions, BTHZ and UDMA-based composites achieved very high DC regardless of the type of ACP filler utilized: $(90.3 \pm 1.2)\%$ (BTHZ), $(89.6 \pm 1.4)\%$ (U132H), $(87.7 \pm 2.1)\%$ (U66H) and $(82.6 \pm 3.0)\%$ (U). However, the DC of TP composites

were significantly lower ($(70.0 \pm 1.6)\%$). Therefore, as formulated, TP composites are more prone to the undesired release of unreacted monomers and are considered inferior to BTHZ or UDMA-based ACP composites.

The relatively low DC of TP composites can primarily be attributed to the structural characteristics of PMGDMA. PMGDMA is actually a tetramethacrylate formed by the reaction of two equivalents of glycerol dimethacrylate (GDMA) and pyromellitic (PM) dianhydride. It is known that conversion typically decreases as the number of reactive groups on a monomer increases. Therefore, because of the rigid aromatic core structure and practically no side-chain flexibility, PMGDMA has only a limited ability to form cross-links. In addition to PMGDMA's rigid structure, hydrogen bonding interactions that involve the carboxylic acid functionalities may also slow the kinetics of polymerization and lead to vitrification at relatively low DC. Bis-GMA, which also has a rigid core structure, exhibits greater flexibility in the polymerization process because it has only two vinyl groups and has weaker hydrogen bonding interactions from its hydroxyl groups compared to the stronger hydrogen bonding interactions of the acidic groups of PMGDMA.

It has been reported [13] that the kinetics of Bis-GMA/TEGDMA co-polymerizations is governed primarily by the Bis-GMA which has a dominant role in the reaction diffusion-controlled termination, a process that becomes rate-controlling as the reaction progresses. Addition of Bis-GMA at mass fraction of 40% or more to TEGDMA [14] resulted in a linear decrease in the final DC. The effect is attributed to the increase in the cure rate, which tends to offset the reduction in resin's mobility. In BTHZ matrices, Bis-GMA was introduced at a mass fraction of 35.5%, and its effect on the overall DC was not that dominant. The high diffusivity of HEMA, however, favors higher DC for resin matrices with relatively high contents of this monomer. Another study of polymerization contraction and conversion of light-cured Bis-GMA-based methacrylate resins [10] showed that, addition of a diluent, monomethacrylate monomer structurally similar to HEMA, i.e. hydroxypropyl methacrylate (HPMA) to Bis-GMA improves the conversion while the increase in contraction remains limited.

Compared to Bis-GMA, UDMA is less viscous, more flexible dimethacrylate with lower strength hydrogen bonding interactions. These factors enhance its cure relative to Bis-GMA. The following reasoning may be used to explain the increasing trend in DC of UDMA-based resins with increasing HEMA content. HEMA, as a monomethacrylate, has a considerably lower polymerization rate than does UDMA. Unlike TEGDMA, both HEMA and UDMA are hydrogen bonding monomers, with the HEMA's OH group forming stronger hydrogen bonds than the urethane groups in

UDMA. Addition of HEMA to UDMA at given concentrations (mass fraction of 6.6% or 13.2%), had only very limited impact on the overall resin mobility and, therefore, HEMA did not slow down the rate of polymerization of U66H and U132H resins.

Multiple factors, such as curing intensity and time, environment temperature, sample size and stress history may have a significant effect on the resulting PS of the samples as evaluated by mercury dilatometer. The standard 60 s/30 s curing mode employed in this study cannot entirely compensate for the heat effects caused by curing light and the rapid exothermic polymerization induced by visible-light irradiation [15]. To eliminate all of the light-generated heat effects a maximum of 0.20% shrinkage should be deducted from PS. However, effects from the exothermic polymerization cannot be easily adjusted. The PS results discussed below are compared without correcting the values for the "light" heat effect; this should not invalidate comparison among different matrices and ACP fillers.

Contrary to DC results which appear to be mainly influenced by the resin formulation and practically independent on the type of the ACP filler, the PS results of the examined composites showed a more complex dependence on both the resin composition and the filler type. Due to its relatively high PS and low DC and the fact that TP composites show inadequate Ca^{2+} ion release caused by calcium binding with free carboxylic functionalities of PMGDMA [16,17], the TP resin does not appear to be a promising matrix phase for ACP composites despite of their potentially enhanced adhesiveness to dentin surfaces compared to BTHZ composites (unpublished results).

Introduction of the hybrid ACPs in BTHZ and/or UDMA composites resulted in variable (or inconsistent) effects on the PS of such composites. However, increase in the PS of hybrid U66H and U132H composites (6.21% and 6.59%, respectively, compared to 4.64% and 4.19% as found in u-ACP controls) as well as high PS of BTHZ composites correlates well with the elevated content of HEMA in these composites. At this point we could only offer a speculative explanation for this effect—the same hydrogen bonding interactions argument as described above. When monomers are polymerized, the free volume decreases and the hydrogen bonding interactions typically become stronger. Consequently, the densification of polymerization is enhanced by the more pronounced hydrogen bonding ability of HEMA in all BTHZ and hybrid ACP/UDMA-based matrices.

Comparison of the PS results reported in this study with recently published PS data on commercially available resin-based composites indicates that the majority of our experimental composites (Fig. 3) shrank more than commercially available highly filled composites whose reported PS ranged between 1.9%

and 4.1% [18,19]. This finding is not surprising considering the fact that our composites had significantly lower filler content (40% in comparison with 77–82% in commercial products) and that ACPs utilized have very heterogeneous size distribution (unpublished data). BTHZ, U, U66H and U132H composites have the PS comparable to commercially available flowable composites (PS between 3.6% and 6.0% [18]). TP, designed as adhesive resin, falls into adhesive resin category (range 6.7–13.5% [18]). One possible way to reduce the PS of these bioactive composites would be by the use of bulkier but relatively low viscosity resins or by increasing the filler content.

5. Conclusion

In this study the degree of vinyl conversion and volumetric contraction of several types of resin composites formulated with three types of amorphous calcium phosphate, were investigated. The conversion of methacrylate functional groups in the resin matrix of the various types of composites was found to be independent of the type of filler phase, but dependent on monomer and the compositional factors of the resin matrix. By contrast, volumetric contraction of these experimental composites appeared to depend not only on the type of resin but also on the type of amorphous calcium phosphate filler, especially in composites derived from the diurethane dimethacrylate base monomer (UDMA) with 2-hydroxyethyl methacrylate (HEMA).

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