Published in final edited form as:
Polym Int. 2007 ; 56(4): 497–505.

Effect of Chemical Structure and Composition of the Resin Phase on Vinyl Conversion of Amorphous Calcium Phosphate-filled Composites

D. Skrtic[1] and **J.M. Antonucci**[2]

1 *Paffenbarger Research Center, American Dental Association Foundation, Gaithersburg, MD 20899, USA*

2 *Polymers Division, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA*

Abstract

The objective of this study was to elucidate the effect of chemical structure and composition of the polymer matrix on the degree of vinyl conversion (DC) of copolymers (unfilled resins) and their amorphous calcium phosphate (ACP) composites attained upon photo-polymerization. The DC can also be an indicator of the relative potential of these polymeric materials to leach out into the oral environment un-reacted monomers that could adversely affect their biocompatibility. The following resins were examined: 1) 2,2-bis[p-(2′-hydroxy-3′-methacryloxypropoxy)phenyl]propane (Bis-GMA)/triethylene glycol dimethacrylate (TEGDMA) (1:1 mass ratio; BT resin) combined with hydroxyethyl methacrylate (HEMA; BTH resin) and with HEMA and zirconyl dimethacrylate (BTHZ resin), 2) urethane dimethacrylate (UDMA)/HEMA resins, and 3) pyromellitic glycerol dimethacrylate (PMGDMA)/TEGDMA (PT resin). To make composite specimens, resins were mixed with a mass fraction of 40 % zirconia-hybridized ACP. Copolymers and their composites were evaluated by near infra-red spectroscopy for DC after 1 d and 28 d post-cure at 23 °C. Inclusion of HEMA into the BT and UDMA resins yielded copolymers and composites with the highest DCs. The significantly lower DCs of PT copolymers and their composites are attributed to the rigid aromatic core structure, tetra-vinyl functionality and limited methacrylate side-chain flexibility of the surface-active PMGDMA monomer. There was, however, an increase in the 28 d DC for the PT materials as there was for the BTHZ system. Surprisingly, the usual decrease observed in DC in going from unfilled polymer to composite was reversed for the PT system.

Keywords

amorphous calcium phosphate; copolymers; composites; degree of vinyl conversion

Introduction

For the last decade our research has focused on utilizing the relatively high solubility of amorphous calcium phosphate (ACP) and its ready conversion to a stable apatitic mineral (1)

Corresponding author: Drago Skrtic, Paffenbarger Research Center, American Dental Association Foundation, National Institute of Standards and Technology, 100 Bureau Drive - Stop 8546, Gaithersburg, MD 20899-8546, Phone: (301) 975-3541, Fax: (301) 963-9143, E-mail: drago.skrtic@nist.gov.

in formulating bioactive polymer-based composites for a variety of potential dental applications (2–5). ACP's bioactivity is seen as particularly advantageous in enhancing the prophylactic performance of such composites by preventing tooth demineralization or by actively promoting remineralization (6).

When ACP is embedded as filler in certain types of polymeric matrices derived from the ambient polymerization of acrylic monomers and the resulting composites are subsequently exposed to aqueous milieu, significant levels of calcium and phosphate ions are released in a sustained manner over long time periods. Given the nature of the ACP filler phase; it is not surprising that the overall mechanical properties of these ACP composites are inferior to conventional, bioinert, silanized-glass-filled dental composites. Glass fillers are mechanically stronger and more resistant to the aqueous environment than the porous, degradable ACP. Additionally, the silane-derived interfacial phase of the glass fillers promotes chemical binding to the polymeric phase, thereby, reinforcing the polymer matrix of the composite. In an effort to improve the mechanical and overall physicochemical performance of ACP composites, several studies were performed to better comprehend the relationship between mechanical strength of the composites, the chemical structure/composition of the resin and the type of the ACP filler utilized (7,8). The use of zirconia-hybridized ACP (Zr-ACP) rather than unmodified ACP yielded composites with moderately improved mechanical strength (3–5). It was previously shown that the chemical structure and composition of certain types of resin matrices affected the ion release and water uptake of composites but had very little effect on the polymerization shrinkage and the mechanical stability of specimens upon aqueous exposure (4,5,7).

The overall objective of this study was to assess the effect of the chemical structure and resin matrix composition on the degree of vinyl conversion (DC), of the unfilled copolymers and their corresponding Zr-ACP composites. Zr-ACP was formulated into composites based on several different matrices containing as base resins 2,2-bis[p-(2′-hydroxy-3′-methacryloxypropoxy)phenyl] propane (Bis-GMA), urethane dimethacrylate (UDMA) or pyromellitic glycerol dimethacrylate (PMGDMA), with co-monomers such as triethylene glycol dimethacrylate (TEGDMA), 2-hydroxyethyl methacrylate (HEMA) and zirconyl dimethacrylate (ZrDMA). The DC attained upon polymerization of these resin matrices can affect the mechanical strength of composites and may sometimes be taken as an indicator of the potential leachability of unreacted monomeric species, and, in turn, the biocompatibility of the composites (4,9). Three types of surface-active monomers were investigated in formulating the resin matrices: 1) the mono-functional hydroxylated monomer, HEMA, that was introduced into Bis-GMA and UDMA resins, 2) ZrDMA that was introduced along with HEMA into Bis-GMA, and 3) the tetra-functional carboxylic monomer, PMGDMA, that was introduced into an equal mass of TEGDMA. A hypothesis tested was that HEMA-containing matrices would yield materials with higher DCs compared to the non-HEMA resins.

Materials and Methods

Synthesis 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 $Ca(NO_3)_2$ solution, a 536 mmol/L Na_2HPO_4 solution that contained a mole fraction of 2 % $Na_4P_2O_7$ (a stabilizing component for ACP (10)) and an appropriate volume of a 250 mmol/L $ZrOCl_2$ solution (mole fraction of 10 % $ZrOCl_2$ based on $Ca(NO_3)_2$). The reaction pH varied between 8.6 and 9.0. The suspension was filtered, the solid phase washed subsequently with ice-cold ammoniated water and acetone, and then lyophilized. To prevent exposure to humidity, Zr-ACP was kept under vacuum (2.7 kPa) until utilized for composite preparation.

The amorphous state of the filler was verified by powder X-ray diffraction (XRD: Rigaku X-ray diffractometer, Rigaku/USA Inc., Danvers, MA, USA) and Fourier-transform infrared spectroscopy (FTIR: Nicolet Magna-IR FTIR System 550 spectrophotometer, Nicolet Instrument Corporation, Madison, WI, USA). Morphology/topology of the filler, after the specimen was sputter-coated with gold, was examined by scanning electron microscopy (SEM; JSM-5400 instrument JEOL Inc., Peabody, MA, USA). 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, USA) following dispersion of the solid in isopropanol and 10 min ultrasonication. Water content of the filler was determined by thermogravimetric analysis (TGA; Perkin Elmer 7 Series Thermal Analysis System, Norwalk, CT, USA). The TGA measurements (3 separate runs) were performed by heating (5 to 10) mg of powdered Zr-ACP at the rate of 20 °C/min over a temperature range of (30 to 600) °C in air. The relative amounts of surface or loosely bound water (the mass loss over the 23 °C to 125 °C interval) and structurally incorporated water (the mass loss over the 150 °C to 600 °C interval) were determined from TGA thermal curves. Ca/PO_4 ratio of the solid after dissolution in HCl was calculated from solution calcium and phosphate concentrations values measured with spectrometric methods (UV/VIS Carey Model 219 spectrophotometer, Varian Analytical Instruments, Palo Alto, CA, USA) (11,12).

Formulation of methacrylate resins

The experimental resins were formulated from the commercially available dental monomers and the components of the photo-initiator system listed in Table 1. The indicated acronyms are used throughout this manuscript. The corresponding chemical structures are presented in Figs. 1a, b. The compositions of all experimental resins are provided in Table 2.

Three types of Bis-GMA/TEGDMA resins based on 1:1 by mass mixtures of Bis-GMA/TEGDMA were formulated (assigned BT, BTH and BTHZ resins). The level of HEMA comonomer in Bis-GMA resin series was chosen to correspond to its concentration in the Bis-GMA-based resins that resulted in high bioactivity (ion release) of the corresponding ACP composites (2,4). Resins based on UDMA, monomer reportedly being more reactive than Bis-GMA (13), were formulated with lower levels of HEMA (U0H, U66H and U132H matrices containing 0 %, 6.6 % and 13.2 % by mass fraction HEMA, respectively). The PT resin consisted of equal masses of the viscous, multifunctional PMGDMA and the low-viscosity TEGDMA.

Bis-GMA- and UDMA based resins were photoactivated by the inclusion of CQ and 4EDMAB (Fig. 1b) as photo-oxidant and photo-reductant, respectively. These resin/initiator systems had excellent storage stability and yielded well-polymerized materials. The simplified oxidation-reduction reaction is shown in Fig. 2a. The amine derived radicals constitute the major initiating radicals. They are formed by electron transfer-hydrogen abstraction reactions involving the excited complex that forms between CQ and the amine. In the PT series, 369 IRGACURE, 4265 DAROCUR and CQ (Fig. 1b) were selected as the photoinitiator system to enhance photo-polymerization and possibly circumvent storage instability that usually is encountered with the use of CQ and 4EDMAB in the resins containing acidic monomers (4). In this case the initiator radicals are produced primarily by a homolytic photo-cleavage although there also may be a minor redox mechanism involved. In any case the ternary component photoinitiator system shown in Fig. 2b yielded resin systems with acceptable storage stability and adequate cure characteristics.

Degree of vinyl conversion (DC)

The near FTIR spectroscopic (NIR) method (14) was employed to determine the DC of copolymers (unfilled resins) and composites specimens. The 6165 cm^{-1} absorption band was

used to assess the conversion in paired monomer and polymer spectra of individual samples. The NIR spectra were obtained from 64 co-added scans at four wave-number resolution with the same instrument as used for the FTIR screening of Zr-ACP solids. For the NIR scanning, the spectrophotometer was configured with a white light source, a CaF_2 beam splitter and an InSb detector.

The NIR spectra of uncured copolymers were collected in a yellow light (flux intensity <753 lux (15)) illuminated room to prevent the unwanted polymerization due to the exposure of the light-sensitive resin to the near UV - blue portion of the spectrum. Teflon molds (diameter = (3.0 to 3.3) mm; thickness = (4.9 to 5.1) mm) were put on a bottom glass slide, filled with resin, covered with a top glass slide and the assembly positioned in a standard sample holder with a 5 mm diameter opening and finally scanned. Each face of the mold assembly was then irradiated for 120 s with visible light (Triad 2000, Dentsply International, York, PA, USA). NIR spectra of cured copolymers were obtained after 1 d (all resins) and also at 28 d for the BTHZ and PT formulations post-cured at 37 °C in the dark.

Composite pastes were prepared by mixing the various resins (Table 2; 60 % by mass fraction) and the Zr-ACP filler (40 % by mass fraction) by hand spatulation (under yellow light (15)). After mixing the resins with Zr-ACP, the pastes were kept under a moderate vacuum (2.7 kPa) at 23 °C for 24 h to eliminate the air entrained during mixing. To collect the spectra of the uncured composites, the pastes were molded into disks (diameter = (15.8 to 19.8) mm; thickness = (1.6 to 1.8) mm) by filling the circular openings of flat Teflon molds, covering each side of the mold with a Mylar film plus a glass slide. The assembly was positioned in a standard FTIR sample holder and the NIR spectrum of the uncured composite obtained. The disks were then photo-polymerized (irradiating conditions identical to those for the copolymer specimens), post-cured for the predetermined time intervals and their spectra collected.

After collecting the NIR spectra, the cured copolymer and composite specimens were disassembled, removed from the molds and their thickness measured by micrometer. By measuring the thickness of monomer/polymer specimens the need to use an invariant absorption band as an internal standard was circumvented. DC (%) was calculated from the decrease in integrated absorption peak area at 6165 cm^{-1}/specimen thickness values utilizing the following formula:

$$DC=\{1-[(\text{area}/\text{thickness})_{\text{polymer}}/(\text{area}/\text{thickness})_{\text{monomer}}]\}\cdot 100 \quad [1]$$

Number of replicate samples in each experimental group was $n \geq 5$.

Statistical data analysis

One standard deviation (SD) is given in this paper for comparative purposes as the estimated standard uncertainty of the measurements. Experimental data were analyzed by ANOVA ($\alpha = 0.05$). Significant differences between specific groups were determined by all pair-wise multiple comparisons (two tail t-test; unequal variances).

Results

The amorphous state of the filler employed in this study was verified by XRD and FTIR. The two diffuse, broad bands typically seen in the XRD spectrum of ACP and the two wide absorption bands in the phosphate stretching region [(1200 to 900) cm^{-1}] and the phosphate bending region [(630 to 500) cm^{-1}] in the typical FTIR spectrum of ACP have been published previously (4,7) and are not shown here. Results of particle size distribution analysis indicate highly heterogeneous ACP particles ranging from sub-μm up to 80 μm values (expressed as the equivalent spherical diameter). Existence of polydispersed aggregates was confirmed by SEM observations; typical morphological/topological features are shown in Fig. 3. The median

diameter (d_m) and the specific surface area (SSA) of the Zr-ACP filler calculated from the 3 independent PSD measurements were: d_m = (7.2 ± 1.8) μm and SSA = (0.52 ± 0.20) m^2/g. Total water content of the powder was a mass fraction 14.9 %, of which approximately 2/3 corresponded to the surface-bound (mobile water) while the remaining 1/3 was structurally incorporated. The Ca/PO_4 ratio of the filler was 1.89 ± 0.10.

The composite paste typically looked as shown in Fig. 4a. An image of the same sample after the photo-curing clearly reveals the non-homogeneity of filler's distribution throughout the composite disk specimen (Fig. 4b). The same pattern was observed in all of the investigated systems regardless of the resin type.

The exemplary NIR spectra of the uncured and cured BT copolymer specimen are shown in Fig. 5. The results of the DC screening of copolymers and composites for all experimental groups are summarized in Figs. 6–9. The analysis of 24 h post-cure DC data in Bis-GMA-based matrices (Fig. 6) revealed the following. The binary, non-HEMA copolymer and composite specimens attained significantly lower conversion ((85.4 ± 2.5) % and (82.1 ± 4.1) %, respectively) than HEMA-containing copolymers and composites (average for BTH and BTHZ formulations: (92.1 ± 2.7) % and (87.2 ± 5.0) %, respectively). A small, but significant reduction in DC (3.8 % to 5.6 %) was observed in all Bis-GMA based composite specimens compared to their corresponding copolymer samples. HEMA had the same effect on the attained DC levels in UDMA-based resin matrices (Fig. 7). The increases in DC (83.9 %, 88.6 % and 90.8 % for U0H, U66H and U132H resins, respectively) with the increasing levels of HEMA were found to be significant for all copolymer specimens. Also significant were the differences in the DC of U0H composites (82.2 %) and both U66H (87.3 %) and U132 (89.0 %) composites. The observed reduction (1.4 % to 2.1 %) in DC of UDMA composite specimens compared to the corresponding copolymers was significant only for U132H formulations. The average DC attained in 24 h post-cure PT copolymer and composite specimens was 66.6 % and 71.8 %, respectively (Fig. 8). These values are between 21 % and 28 % lower than the DC obtained in Bis-GMA and UDMA copolymer series and between 13 % and 19 % lower than the DC values of Bis-GMA and UDMA composites. However, a surprising finding was the higher DC value of the PT composite compared to the PT copolymer

The effect of post-curing time on the DC in PT and BTHZ resin matrices is presented in Figs. 8 and 9, respectively. In both systems DC increased significantly with aging. The extent of the increase was higher in PT matrices (15.7 % for copolymers and 16.3 % for composites) compared to BTHZ resins (5.2 % for copolymers and 8.4 % for composites). Again, a reversal was noted in the usual order of relative DC values [copolymer = composite] for the PT materials [composite > copolymer].

Discussion

The resin systems containing HEMA, i.e., the BTH, BTHZ, U66H and U132H resin, showed the highest DC in both unfilled copolymers and composites, probably because of the high diffusivity and mono-functionality of HEMA. The effect is expected to become more dominant as the HEMA content increases; such a trend was indeed seen in the UDMA resin series. A similar effect DC-enhancing effect has been reported for Bis-GMA based resins that contained hydroxypropyl methacrylate (HPMA; a monomer homologous to HEMA) as a diluent co-monomer (16). Introduction of HPMA had no adverse effect on the volumetric polymerization shrinkage (PS) of the resins. It is, theoretically, expected that high DC would result in elevated PS values, leading to the formation of unwanted gaps and stress sites both within the composite and at the composite/tooth boundary (17–19). UDMA resins were previously screened for PS by utilizing computer-controlled mercury dilatometry (4). As the DC of U0H, U66H and U132H composites increased with the increasing HEMA content, their PS also increased from

(4.2 ± 0.5) vol % to (5.6 ± 0.3) vol % to (6.4 ± 0.5) vol %, respectively. The relatively high PS of these composites may help promote micro-leakage and, therefore, compromise the potential clinical application of these composites despite their favorable DC levels.

The relatively lower DC of the PT copolymer and its composite compared to those derived from Bis-GMA and UDMA based matrices is primarily attributed to the chemical structural characteristics of PMGDMA (20). Probably most of the residual vinyl un-saturation is in the form of pendant vinyl groups attached to the polymer matrices rather than unreacted PMGDMA. Any residual monomer is more likely to be in the form of TEGDMA. PMGDMA has rigid aromatic core structure with relatively non-flexible side chains that have two types of reactive functional groups, four vinyl and four carboxylic both leading to its limited ability to form highly converted cross-linked networks. Furthermore, PMDGMA's carboxylic groups exhibit strong hydrogen bonding interactions and even ionic binding reactions with the ACP filler limiting its diffusion and participation in polymer network formation. These structural factors may slow the polymerization kinetics and cause vitrification of the PT resin at relatively low DCs. To limit the effect of excessive ionic bonding interactions with ACP, enhance DC of the network matrix, optimize intracomposite adhesion and bonding to tooth structure, resin formulations should contain significantly reduced levels of PMGDMA. The actual amounts should be determined by a battery of physicochemical tests involving, besides the DC screening, the mechanical strength measurements, shear bond strength assessments to tooth structure and remineralization potential evaluation. The latter parameter is of particular importance since the PT polymeric matrix can bind calcium released from ACP/PT composites upon aqueous exposure, therefore compromising their remineralizing ability (21).

For the Bis-GMA and UDMA based polymeric materials, the observed reduction in DC in going from copolymer to 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 particle size distribution of the ACP filler) also may contribute to this reduction. The significant reverse trend observed in PT copolymers and composites could be explained by strong, intermolecular hydrogen bonding and by the greater affinity of PMGDMA co-monomer's acid functionalities for ACP filler resulting in higher interfacial conversion of methacrylate groups (because of the favorable alignment of some of these groups for copolymerization with TEGDMA) compared to the other copolymer systems.

Presumably, the increase in DC observed after 28 d is probably a result of the diffusion of the more mobile TEGDMA rather than the relatively immobilized PEGDMA to PT copolymer network. However, the ability of the highly surface-active PEGDMA to form strong hydrogen bonds in the developing copolymer matrix, and also to strongly interact ionically with ACP, can cause a more favorable alignment of its vinyl groups that may promote significant postcure leading to the dramatic increase in DC after 24 h and 28 d. A similar but somewhat less dramatic increase in DC for the copolymer and composite based on BTHZ matrix also occurred after 24 h, which may be partially due to the surface-active nature of ZrDMA.

Another factor that may affect the DC results is the different initiator system used in the PT resin compared to the usual CQ/4EDMAB redox photo-initiator.

Numerous factors apparently affect the DC and, consequently, the development of contraction stresses in dental composites. These factors can be separated into material formulation factors (monomer chemistry, monomer structure, filler type, filler content) and material polymerization factors (polymerization rate, type and concentration of the photoinitiator system, curing method, etc.). Different approaches have been proposed to address the great complexity of this problem (18,19,22–25). It is known that DC, elastic modulus, curing rate

and the boundary conditions all considerably affect the magnitude of the contraction upon polymerization. It is, however, difficult to prepare copolymer and/or composite formulations that can successfully isolate only one variable. As an example, if one modifies the content of the filler to vary the elastic modulus, the polymerization shrinkage will be affected due to the altered resin content. Or, by simply varying the curing time the DC of copolymers and composites will typically be affected. Therefore, it appears that only a comprehensive physicochemical screening that includes a battery of physicochemical tests (polymerization shrinkage and stress development, mechanical property evaluation, ion release profile, and water sorption, in addition to DC assessment) could lead to reliable conclusions regarding the clinical utility of newly designed experimental dental materials. Hence, the DC data described in this study should only be taken as one predictor of the expected material's behavior under physiological/oral conditions. The true test of the effectiveness of the structure/property approach must comprise a wider spectrum of property assessments, including, ultimately, clinical trials. In future studies we plan to determine if significant amounts of residual resins are present in the polymerized specimens. Long-term immersion of the various specimens in good solvents for the resin matrix phase followed by analysis of extractables by liquid chromatography, Fourier-transform infrared spectroscopy and/or nuclear magnetic resonance spectroscopy will be used. Similar studies employing aqueous immersion media also will be utilized if significant leachables are found after the immersion experiments in organic solvents.

Conclusions

The DC attained in copolymers (unfilled resins) and their corresponding Zr-ACP composites strongly depended on the compositional makeup of the matrix, especially the chemical structure of the surface active monomers utilized to formulate the resin. The inclusion of HEMA, a surface-active, mono-functional co-monomer of low viscosity into Bis-GMA/TEGDMA and UDMA resins helped in attaining higher levels of DC. The 24 h DC attained in the resins containing the surface-active PMGDMA and TEGDMA was lower than that of the Bis-GMA and UDMA resins due to the PMGDMA's high viscosity, rigid aromatic core structure, low side-chain flexibility and poor diffusivity due to the highly polar character of its carboxylic acid groups, especially after interaction with ACP. The ability of the carboxylic groups of PMGDMA monomer to strongly hydrogen bond during formation of the matrix and also strongly interact with Zr-ACP probably accounts for the significant increase in DC after 28 d post-cure for both the copolymer and its composite. It is not understood at this point why the conversion of the PMGDMA/TEGDMA composite exceeded that of the unfilled copolymer but it may indicate that PMGDMA reacts with ACP to favorably align its methacrylate so that copolymerization and, therefore, DC is enhanced. A similar but less dramatic enhancement of DC with post-cure was observed for copolymers and their composites derived from a resin containing Bis-GMA, TEGDMA, HEMA with a small amount of the highly polar, surface-active zirconyl dimethacrylate.

Acknowledgements

This investigation was supported by the research grant DE13169-07 to the American Dental Association Foundation from the National Institute of Dental and Craniofacial Research. We are grateful to Esstech, Essington, PA, USA for the generous donation of Bis-GMA, TEGDMA, UDMA, HEMA and PMGDMA monomers.

References

1. Eanes, ED. Amorphous calcium phosphate: thermodynamic and kinetic considerations. In: Amjad, Z., editor. Calcium phosphates in biological and industrial systems. Kluwer Academic Publishers; Boston: 1998. p. 21-39.
2. Skrtic D, Antonucci JM, Eanes ED, Eichmiller FC, Schumacher GE. J Biomed Mat Res (Appl Biomater) 2000;53:381–391.

3. Skrtic D, Antonucci JM, Eanes ED, Brunworth RT. J Biomed Mater Res 2002;59:597–604. [PubMed: 11774320]
4. Skrtic D, Antonucci JM, Eanes ED. J Res Natl Inst Stand Technol 2003;108:167–182.
5. Skrtic D, Antonucci JM, Eanes ED, Eidelman N. Biomaterials 2004;25:1141–1150. [PubMed: 14643587]
6. Skrtic D, Hailer AW, Takagi S, Antonucci JM, Eanes ED. J Dent Res 1996;75(9):1679–1686. [PubMed: 8952621]
7. Antonucci JM, Skrtic D. J Bioact Comp Polym 2005;20:29–49.
8. Antonucci, JM.; Skrtic, D. Physicochemical properties of bioactive polymeric composites: Effects of resin matrix and the type of amorphous calcium phosphate filler. In: Shalaby, SW., editor. Polymers for dental and orthopedic applications. CRC Press; Boca Raton: 2006. in press
9. Simon CG, Antonucci JM, Liu DW, Skrtic D. J Bioact Comp Polym 2005;20:279–295.
10. Eanes ED, Gillessen H, Posner AS. Nature 1965;208:365–367. [PubMed: 5885449]
11. Vogel GL, Chow LC, Brown WE. Caries Res 1983;7:23–31. [PubMed: 6571804]
12. Murphy J, Riley JP. Anal Chim Acta 1962;27:31–36.
13. Stansbury JW, Dickens SH. Polymer 2001;42:6363–6369.
14. Stansbury JW, Dickens S. Dent Mater 2001;17:71–79. [PubMed: 11124416]
15. www.circuitree.com/CDA/ArticleInformation.
16. Venhoven BAM, de Gee AJ, Davidson CL. Biomaterials 1993;14(11):871–875. [PubMed: 8218741]
17. Lu H, Stansbury JW, Dickens SH, Eichmiller FC, Bowman CN. J Mater Sci Mater Med 2004;15:1097–1105. [PubMed: 15516870]
18. Braga R, Ferracane JL. J Dent Res 2002;81:114–117. [PubMed: 11827255]
19. Davidson CL, Feilzer AJ. J Dent 1997;25:435–440. [PubMed: 9604575]
20. Skrtic D, Stansbury JW, Antonucci JM. Biomaterials 2003;24:2443–2449. [PubMed: 12695071]
21. Skrtic D, Antonucci JM, Eanes ED. Polym Adv Technol 2001;12:369–379.
22. Carvalho RM, Pereira JC, Yoshiyama M, Pashley DH. Oper Dent 1996;21:17–24. [PubMed: 8957911]
23. Davidson CL, de Gee AJ. J Adhes Dent 2000;2:167–173. [PubMed: 11317390]
24. Sakaguchi RL. Compend Cont Educ Dent Suppl 1999;25:516–523.
25. Ferracane JL. Dental Mater 2005;21:36–42.

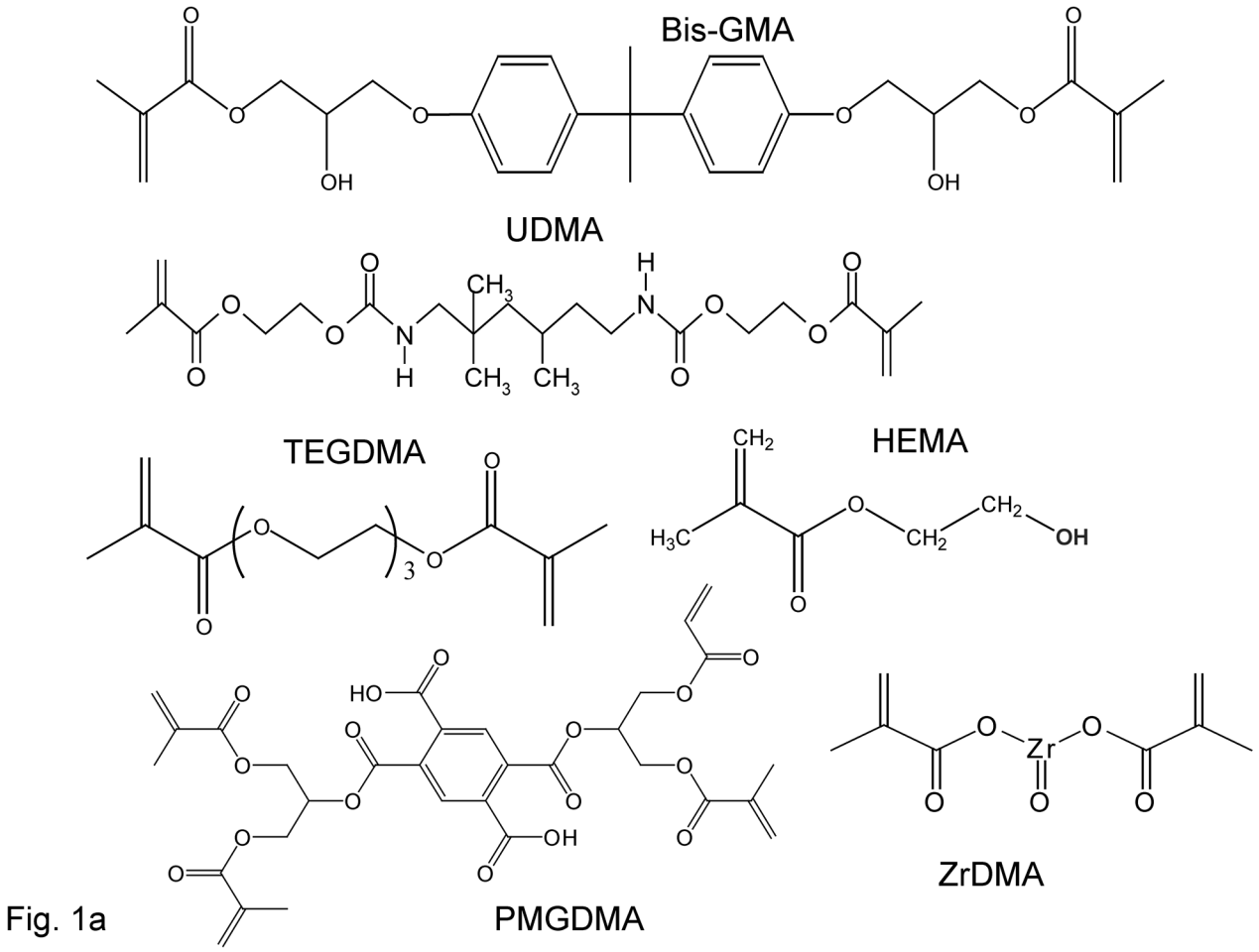


Fig. 1a

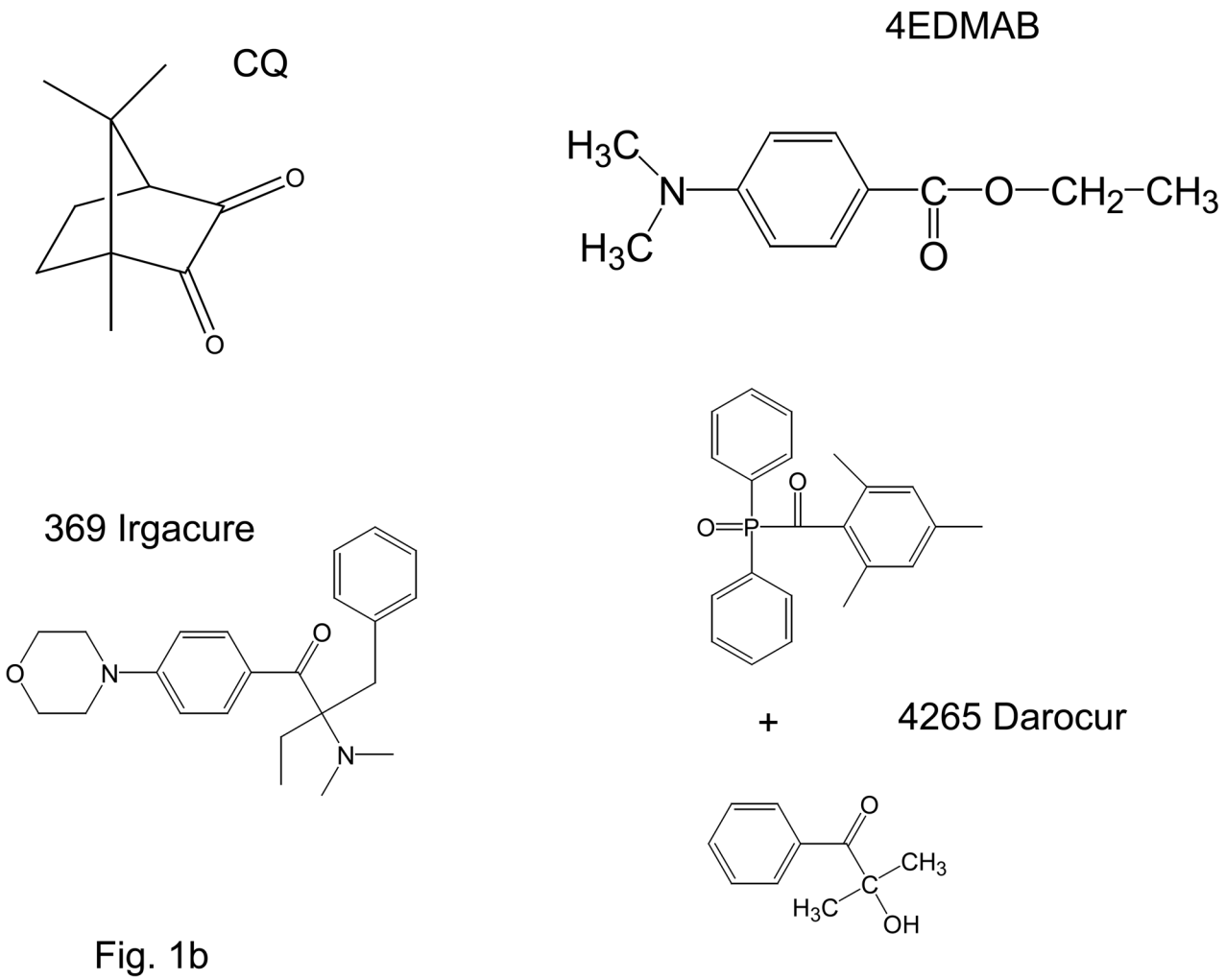
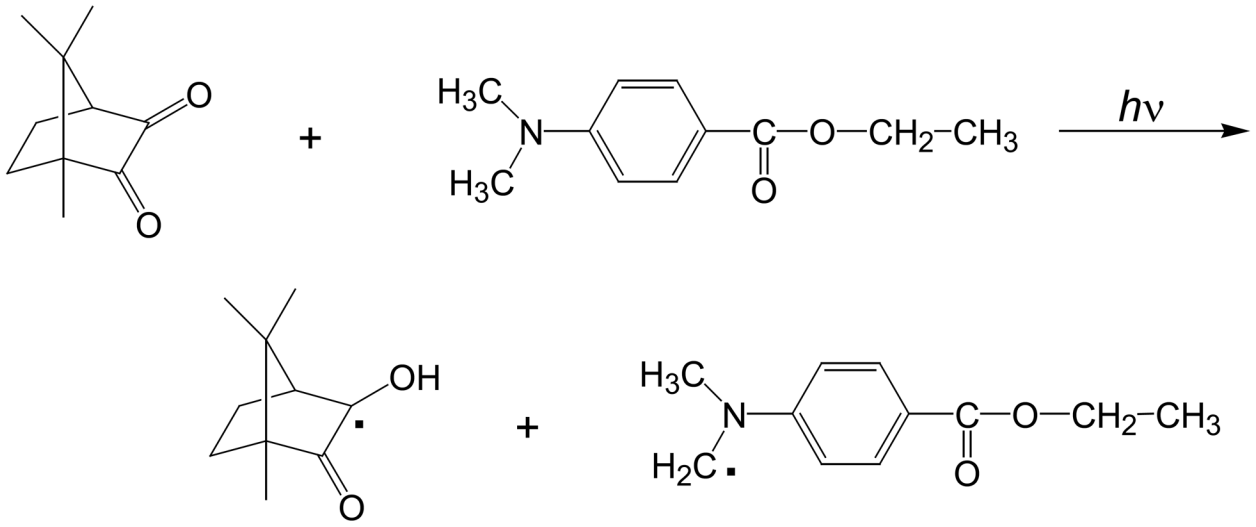


Fig. 1.
Chemical structure of the monomers (a) and the components of photoinitiator systems (b) employed in the study.



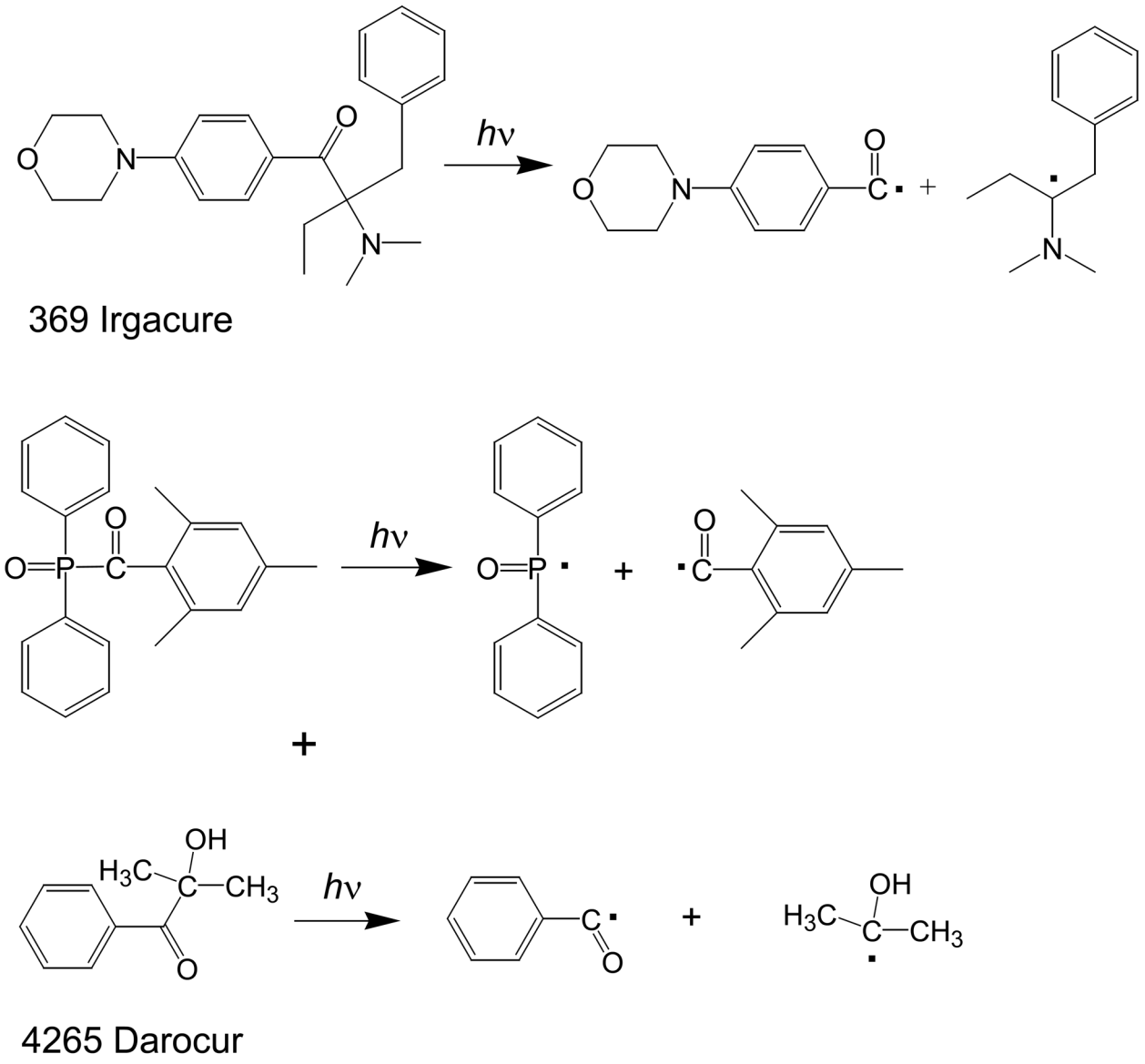


Fig. 2.
Schematic presentation of the photinitiator reaction: CQ and 4EDMAB (part a), 4265 DAROCUR and 369IRGACURE (part b).

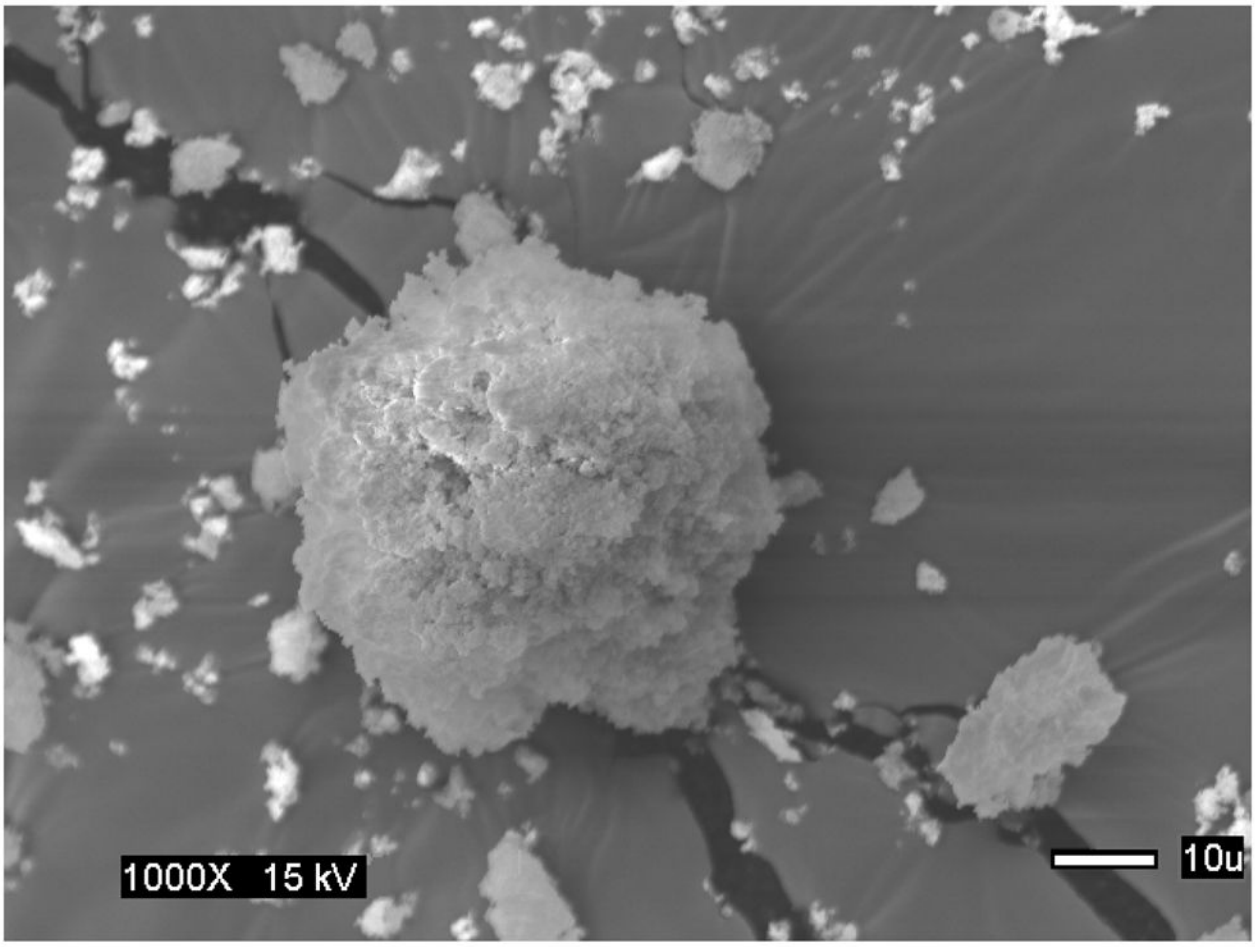


Fig. 3.
Scanning electron microscope image of Zr-ACP utilized in the study.

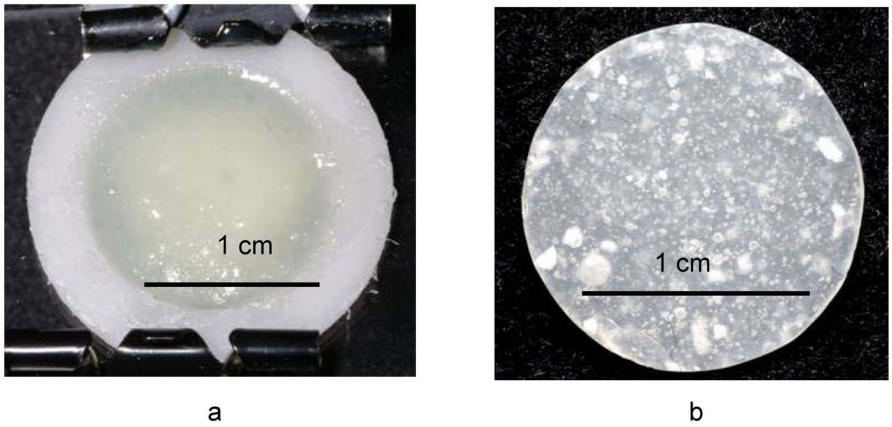


Fig. 4.
Optical photograph of the uncured (a) and cured (b) BTHZ composite specimen. Numerous defects/voids seen in the cured composite disk are also seen in UDMA and TP specimens.

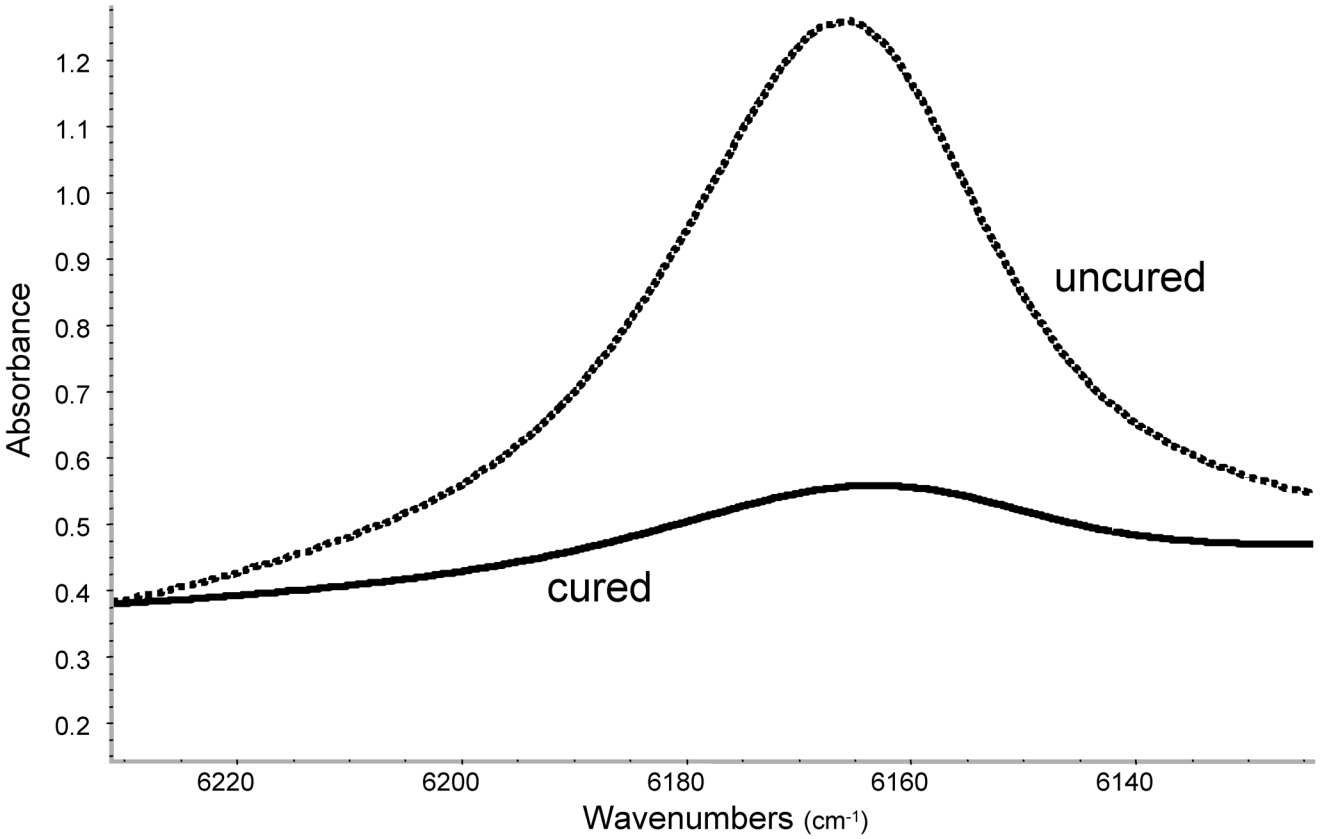


Fig. 5.
The exemplary NIR spectra of the uncured and cured Bis-GMA/TEGDMA unfilled resin (copolymer) specimen; the calculated degree of conversion, DC = 83.3 %.

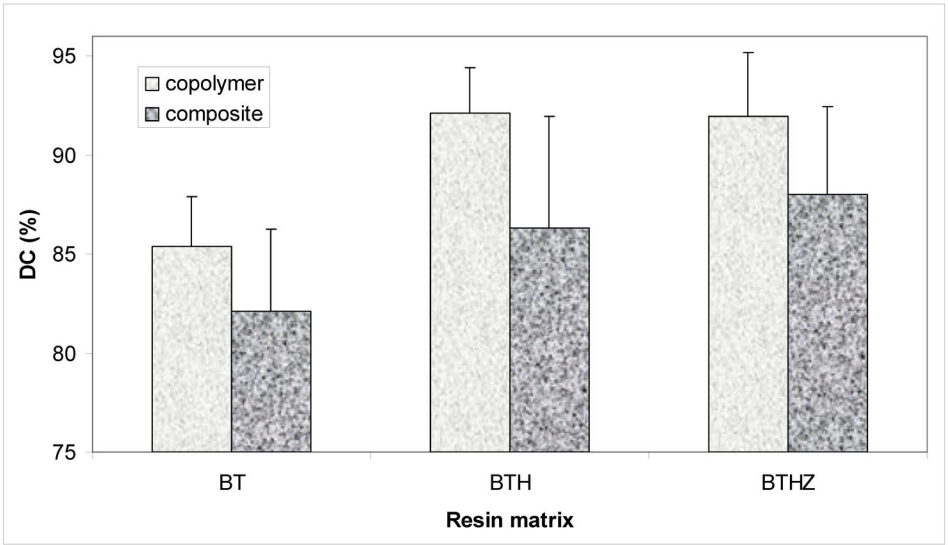


Fig. 6.

Degree of vinyl conversion (DC; mean + standard deviation (SD; indicated by bar)) of Bis-GMA specimens (copolymers and composites) attained 24 h after photo-curing. The number of specimens in each experimental group $n \geq 5$.

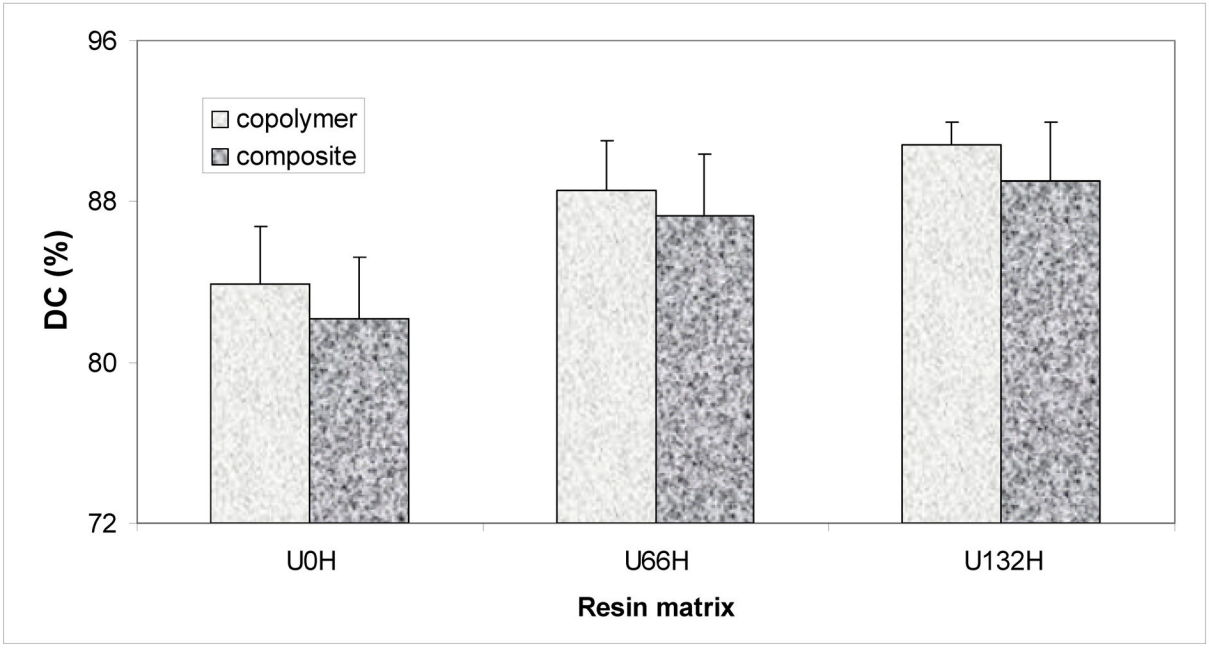


Fig. 7.
DC of UDMA-based copolymers and composites (mean + SD) attained 24 h after photo-curing. Number of specimens n = 8/group.

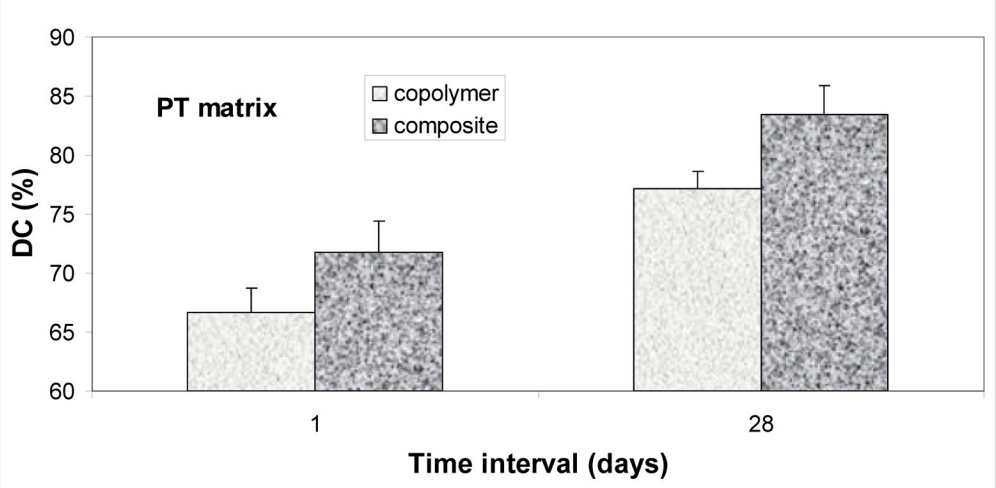


Fig. 8.
Effect of post-curing time on DC attained in an unfilled and ACP-filled Bis-GMA-based matrix.

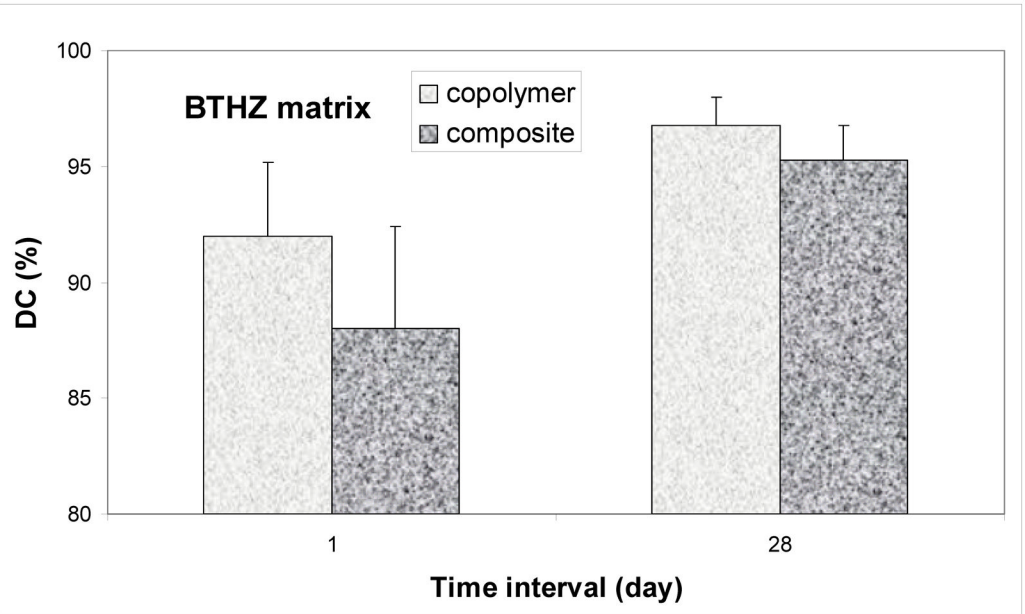


Fig. 9.
Effect of post-curing time on DC attained in an unfilled and ACP-filled TP matrix.

Table 1

Monomers and photoinitiators employed in resin formulations.

Chemical name	Acronym	Manufacturer
2,2-bis[p-(2′-hydroxy-3′-methacryloxypropoxy)phenyl] propane	Bis-GMA	Esstech, PA, USA
Triethylene glycol dimethacrylate	TEGDMA	Esstech, PA, USA
Urethane dimethacrylate	UDMA	Esstech, PA, USA
2-hydroxyehyl methacrylate	HEMA	Esstech, PA, USA
Pyromellitic glycerol dimethacrylate	PMGDMA	Esstech, PA, USA
Zirconyl dimethacrylate	ZrDMA	Aldrich, WI, USA
Camphorquinone	CQ	Aldrich, WI, USA
Ethyl-4-N,N-dimethylaminobenzoate	4EDMAB	Aldrich, WI, USA
Diphenyl-(2,4,6-trimethylbenzoyl)phosphine oxide & 2-hydroxy-2-methyl-1-phenyl-1-propanone	4265DAROCUR	Ciba-Geigy, NY, USA
2-benzyl-2-(dimethylamino)-1-(4-(4-morpholinyl) phenyl-1-butanone	369IRGACURE	Ciba-Geigy, NY, USA

Table 2

Composition (mass fraction %) of experimental resins evaluated in the study.

Component/resin	BT	BTH	BTHZ	U0H	U66H	U132H	PT
Bis-GMA (B)	49.50	35.50	35.50	-	-	-	-
TEGDMA (T)	49.50	35.50	35.50	-	-	-	48.65
HEMA (H)	-	28.00	27.00	-	6.60	13.20	-
UDMA (U)	-	-	-	99.00	92.40	85.80	-
PMGDMA (P)	-	-	-	-	-	-	48.65
ZrDMA (Z)	-	-	1.00	-	-	-	-
CQ	0.20	0.20	0.20	0.20	0.20	0.20	0.40
4EDMAB	0.80	0.80	0.80	0.80	0.80	0.80	-
4265DAROCUR	-	-	-	-	-	-	0.80
369IRGACURE	-	-	-	-	-	-	1.50