

EFFECT OF POLYMER MATRICES ON METHACRYLATE CONVERSION AND MECHANICAL STRENGTH OF BIOACTIVE COMPOSITES BASED ON AMORPHOUS CALCIUM PHOSPHATE

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Introduction

Synthetic calcium phosphates (CaPs) of various types are finding increasing use in the treatment of defective mineralized tissues. Amorphous calcium phosphate (ACP), a unique form of CaP that lacks the long-range, periodic atomic scale order of crystalline CaPs, is a plausible precursor in the formation of biological hydroxyapatite (HAP) - the structural prototype of the mineral component of bones and teeth. Relative to HAP, ACP is more soluble and readily transforms into HAP. We have recently started evaluating ACP as bioactive filler phase in dental composites that utilize typical photocurable dental monomers, e.g. 2,2-bis[p-(2'-hydroxy-3'-methacryloxypropoxy)phenyl] propane (Bis-GMA), triethylene glycol dimethacrylate (TEGDMA) and 2-hydroxyethyl methacrylate (HEMA) as the resin matrix binder phase (1). Significantly, these bioactive composites have demonstrated sustained release of calcium and phosphate ions through the composite microstructure into simulated saliva milieus leading to HAP formation. Such composites should be capable of repairing demineralized tooth structures by inducing mineral recovery via HAP deposition (2).

Previous studies have shown that certain variations in the chemical structure and composition of the resin phase may affect the rate and extent of calcium and phosphate ion release from ACP-filled polymers (3). It also was shown that the use of hybrid ACPs, e.g. those containing silicon (Si) or zirconium (Zr) compounds in their structures, yielded bioactive composites with improved mechanical strength (4). The objective of this study was to assess the effects of chemical structural variations of the most hydrophilic monomeric component, e.g. HEMA, of a Bis-GMA/TEGDMA ternary resin system on the degree of methacrylate conversion (DC) and on the biaxial flexure strength (BFS) of the various ACP composites.

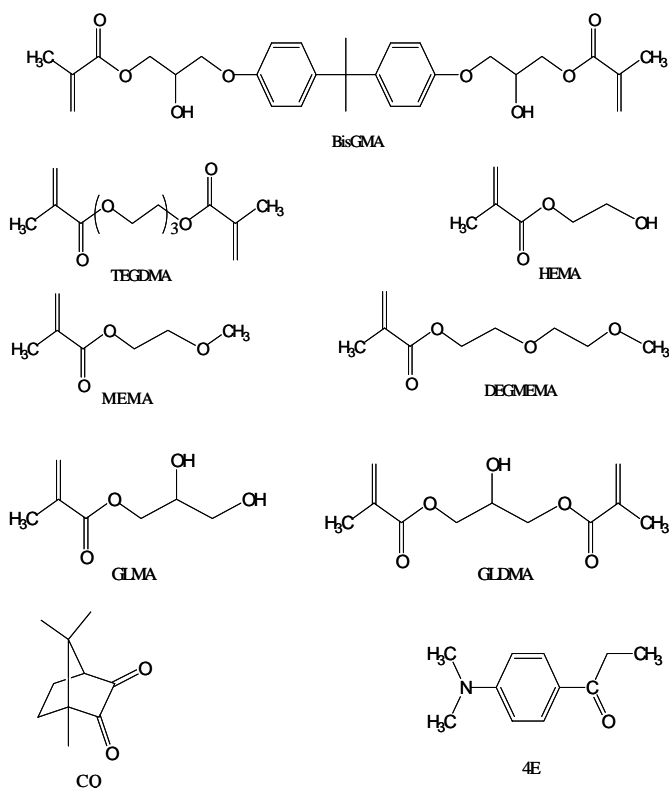
Experimental*

Formulation of Photoactivated Matrix Resins. Five types of photoactivated resins (**Table 1**) based on mixtures of Bis-GMA/TEGDMA (1:1 mass ratio) with a third more hydrophilic monomer (X) were formulated. Equivalent molar masses of either HEMA (**R1**), 2-methoxyethyl methacrylate (MEMA) (**R2**), di(ethyleneglycol)methyl ether methacrylate (DEGMEMA) (**R3**), glyceryl monomethacrylate (GLMA) (**R4**) or glyceryl dimethacrylate (GLDMA) (**R5**) were added to Bis-GMA/TEGDMA along with a visible light photoinitiator system consisting of camphorquinone (CQ) and ethyl-4-N,N-dimethylaminobenzoate (4E).

Table 1. Composition of the Ternary Monomer Systems Used for the Preparation of ACP Composites (mass fraction, %).

	R1	R2	R3	R4	R5
Bis-GMA	37.00	35.65	31.50	34.00	27.50
TEGDMA	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
4E	0.80	0.80	0.80	0.80	0.80

The chemical structures of the monomers and photoinitiator system used in this study are shown below.



Preparation of Zirconium-hybridized ACP. ACP filler was synthesized employing the protocol proposed by Eanes *et al.* (5). Zirconium-hybridized ACP (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 % of Na₄P₂O₇, as a stabilizing component for ACP, and an appropriate volume of a 250 mmol/L ZrOCl₂ solution (mole fraction of 10 % ZrOCl₂ based on Ca reactant). The reaction pH was between 8.6 and 9.0. The suspension was filtered, the solid phase washed with ice-cold ammoniated water and lyophilized. The ACP powder, shown to be amorphous by X-ray diffractometry and Fourier-transform infrared spectroscopy (FTIR), was then evaluated as a filler in composites at a mass fraction of 40 %.

The photoactivated resins and their composite disks were polymerized with the aid of visible light (470 nm) in Teflon molds (15.8 mm to 19.6 mm in diameter and 1.55 mm to 1.81 mm thick). Each face of the mold assembly was irradiated with a visible light source for 120 s (Triad 2000: Dentsply, York, PA).

Mid-FTIR was used to determine the DC of the unfilled resins and their ACP-filled composites by monitoring changes in the 1637 cm⁻¹ absorption band for the vinyl group against that of the phenyl ring at 1582 cm⁻¹ (used as internal standard) 24 h at 23 °C after photo-curing. Triplicate measurements were performed for each experimental group.

BFS values of the dry and wet (after 2 weeks of immersion in HEPES-buffered, pH = 7.40, saline solutions) 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) operated by Testworks4 software. The BFS was calculated according to mathematical expressions given in ref. (6).

Experimental data were analyzed by multifactorial ANOVA ($\alpha = 0.05$). To determine significant differences between specific groups all pairwise multiple comparisons (Student's t-test) were performed.

Results and Discussion

Levels of vinyl conversion after 24 h attained with both unfilled resins and their ACP-composites strongly depended on the resin composition. DC of the unfilled ternary Bis-GMA:TEGDMA:X resin systems (R1-R5) decreased

in the following order [R3] DEGMEMA > ([R1] HEMA, [R2] MEMA) > [R4] GLMA > [R5] GLDMA (Fig. 1.)

Introduction of ACP filler significantly reduced the DC of HEMA-, MEMA- and DEGMEMA-containing composites (16.6 %, 31.2 % and 14.6 %, respectively) compared to corresponding unfilled resins. However, the differences between the DC of GLMA- and GLDMA- resins and composites (7.8 % and 6.3 %, respectively) were statistically insignificant. The reduction in DC in going from unfilled polymer to composite is most likely due to the reduction in the exotherm of resin polymerization by the ACP filler phase, although other factors such as greater air entrapment and light scattering by ACP also may contribute to this reduction.

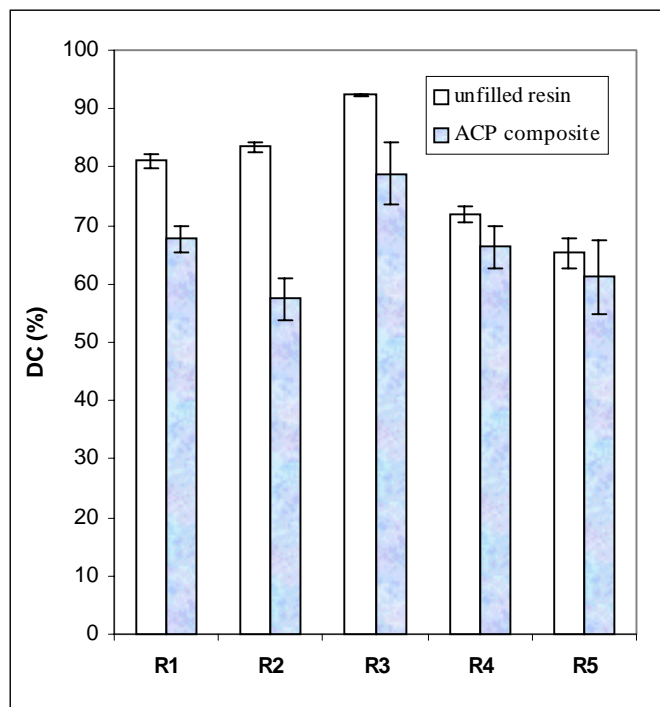


Figure 1. Degree of methacrylate conversion (DC; mean \pm SD (indicated by bars) of unfilled and ACP-filled resins attained at 24 h after photo-curing. The SD is taken as a measure of the standard uncertainty.

BFS values of dry and wet composites are given in Fig. 2. The BFS of all dry composite specimens were on average (67 ± 5) MPa compared to an overall value (28 ± 4) MPa of all the wet composites. There does not appear to be a simple correlation between DC and the dry BFS values. However, exposure to aqueous environment drastically reduced the mechanical strength of the composites. Compared to the dry specimens, the BFS values of the wet composite specimens decreased between 49 % (R4) and 65 % (R5). This reduction in mechanical strength is plausibly caused by a reduction in ACP intactness and rigidity at the ACP-matrix interface because of chemical and, in turn, spatial changes that occurred during the loss of ACP and/or internal conversion to HAP. Excessive water absorption also can cause strength reduction via polymer matrix plasticization. Reduction in the level of the hydrophilic monomer seems necessary to improve the mechanical properties of these composites during aqueous exposure.

Conclusions

The monomer system based on DEGMEMA showed the highest DC both in the unfilled polymer and its composite. The addition of ACP generally resulted in a reduction of DC, but the differential in conversion for polymer and composite for the GLMA- and GLDMA-resins was significantly smaller than for the other resin systems. However, no correlation was observed between DC and the BFS values of the composites, dry or wet. Aqueous exposure always resulted in a significant decrease in BFS.

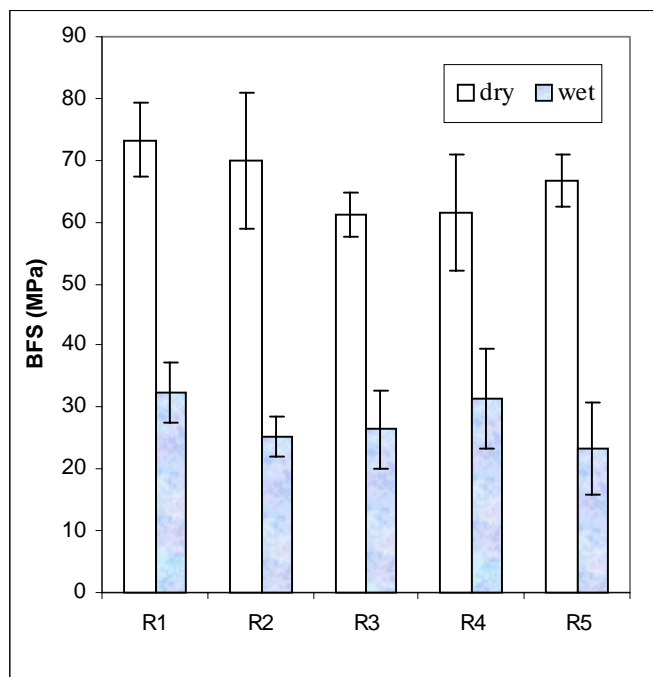


Figure 2. Biaxial flexure strength (BFS; mean \pm SD (indicated by bars) of dry and wet composite specimens. The SD is taken as a measure of the standard uncertainty.

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Disclaimer. Certain commercial materials and equipment are identified in this article to specify the experimental procedure. 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 or equipment identified is necessarily the best available for the purpose.

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