Methacrylate Conversion in Photo-polymerized Composites Containing Amorphous Calcium Phosphate Fillers

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INTRODUCTION

Recently a new class of photocurable composites has been developed that utilizes amorphous calcium phosphate (ACP) as the filler phase with photoactivated dental monomer systems, such as 2,2-bis[p-(2'-hydroxy-3'-methacryloxypropoxy)phenyl]propane (Bis-GMA), triethylene glycol dimethacrylate (TEGDMA) and 2-hydroxyethyl methacrylate (HEMA), providing the resin matrix binder phase (1). ACP, a plausible precursor in the formation of biological hydroxyapatite (HAP), has high solubility in aqueous environments and undergoes facile conversion to HAP, thereby making ACP a potential remineralizing agent. Such ACP-filled composites are envisioned to be bioactive, because they show sustained release of calcium and phosphate ions, and thus are capable of repairing demineralized tooth structures by inducing mineral recovery via HAP deposition.

A previous study has shown that certain variations in the chemical structure and composition of the resin phase may affect the rate and extent of the ion release from ACP-filled composites (2). It has also been found that the use of hybrid ACPs, e.g. those containing silicon (Si) or zirconium (Zr) compounds, can yield similar bioactive composites but with improved mechanical strength.

Although the filler phase and its leachable products are probably biocompatible, there is concern about the biocompatibility of the resin system of these composites. The objective of this study was to evaluate the effects of structural and compositional variations of the resin system on the degree of methacrylate conversion (DC) of ACP composites. Resin compositions that achieve high DCs are expected to exhibit minimal resin leachability, and thereby enhance the biocompatibility of their ACP composites.

EXPERIMENTAL*

Three groups of photoactivated resins based on Bis-GMA, ethoxylated bisphenol A dimethacrylate (EBPADMA) and urethane dimethacrylate (UDMA) were prepared and evaluated for their DC. TEGDMA, 1,6-hexamethylene dimethacrylate (HmDMA) and HEMA were used as comonomers for these base monomers (Table 1a,b,c). A photoinitiator system consisting of camphorquinone (mass fraction 0.2 %) and ethyl-4-N,N-dimethylaminobenzoate (mass fraction 0.8 %; Aldrich, Milwaukee, WI) was used in all resin formulations.

ACP fillers were synthesized employing the protocol proposed by Eanes *et al.* (3). ACP precipitated instantaneously in a closed system at 22 ^{o}C upon rapidly mixing equal volumes of a 800 mmol/L $Ca(NO_3)_2$ solution and a 536 mmol/L Na_2HPO_4 solution that contained a mole fraction of 2 % of $Na_4P_2O_7$, as a stabilizing component for ACP. The reaction pH was maintained between 10.5 and 11.0. This ACP is designated unmodified ACP (u-ACP). Tetraethoxysilane (TEOS)- and zirconyl chloride ($ZrOCl_2$)-hybridized ACPs (Si-ACP and Zr-ACP, respectively) were prepared by simultaneously adding appropriate volumes of either TEOS solution or $ZrOCl_2$ solution and $Ca(NO_3)_2$ solution to the Na_2HPO_4 solution. The reaction pH was maintained between 9.0 to 9.3 and 8.6 to 9.0 for the preparation of Si-ACP and Zr-ACP, respectively. The suspensions were filtered, the solid phase washed with ice-cold ammoniated water and lyophilized. The ACP powders were characterized by X-ray diffractometry and Fourier-transform infrared spectroscopy, and then evaluated in composites with a mass fraction of 40 % filler. Composite pastes were polymerized by visible light in teflon molds (15.8 mm to 19.6 mm in diameter and 1.55 to 1.81 mm thick) sandwiched between mylar covered glass slides. Each face of the mold assembly was irradiated with visible light for 120 s (Triad 2000: Dentsply, York, PA) to form the composite disks.

Table 1a. Bis-GMA-based Resins (mass fraction, %).

	BT	BHm	BTH	BHmH
Bis-GMA	49.50	52.44	35.50	36.97
TEGDMA	49.50	-	35.50	-
HmDMA	-	46.56	-	32.83
HEMA	-	-	28.00	29.20

Table 1b. EBPADMA-based Resins (mass fraction, %).

	ET	EHm	ETH	EHmH
EBPADMA	46.70	49.57	32.90	34.33
TEGDMA	52.30	-	36.93	-
HmDMA	-	49.43	-	34.23
HEMA	-	-	29.17	30.44

Table 1c. UDMA-based Resins (mass fraction , %).

	UT	UHm	UTH	UHmH
UDMA	48.82	51.75	34.83	36.24
TEGDMA	50.18	-	35.85	-
HmDMA	-	47.25	-	33.30
HEMA	-	-	28.32	29.46

Near infrared spectroscopy (6165 cm^{-1} absorption band for vinyl group) was used to determine the mean DC of the resin, polymer or composite (4). The number of specimens for each condition was 9, and the mean values along with standard deviations are indicated in Figs. 1a-d.

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

RESULTS

In all resin groups, HEMA-containing unfilled resins achieved higher DC than the non-HEMA systems. Compared to the unfilled resins, the mean DC of the corresponding ACP-filled composites was generally lower, except for the BT (82 %), ETH (91 %) and UTH (91 %) composites, regardless of the type of ACP filler used (Figs. 1a-d). Thus, there was no clear-cut trend on the effect of filler type on the conversion of the resin, except perhaps with regard to some of the composites formulated with HmDMA, e.g. BHm and EHm resins, which showed rather low conversions with all ACP fillers.

CONCLUSION

EBPADMA or UDMA with TEGDMA/HEMA comonomers yielded the highest DC values for both unfilled resins and composites. Based on the DC results of this study, such ACP-filled composites are expected to have the lowest potential for leaching organic species, and as a consequence, should have better potential for improved biocompatibility.

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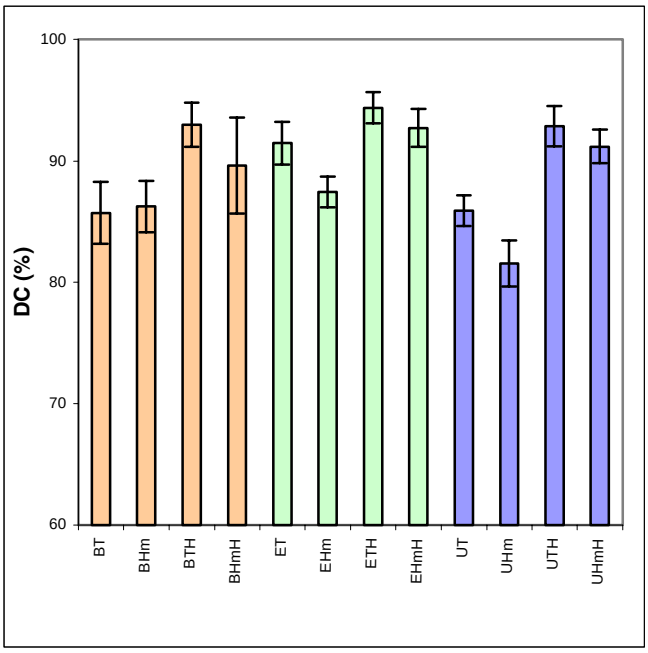

Fig. 1a. DC of unfilled resins.

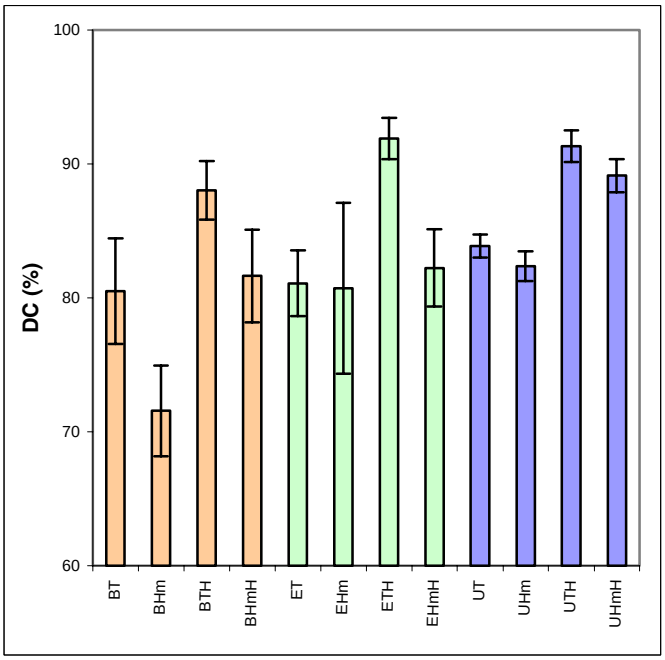

Fig. 1b. DC of u-ACP filled composites.

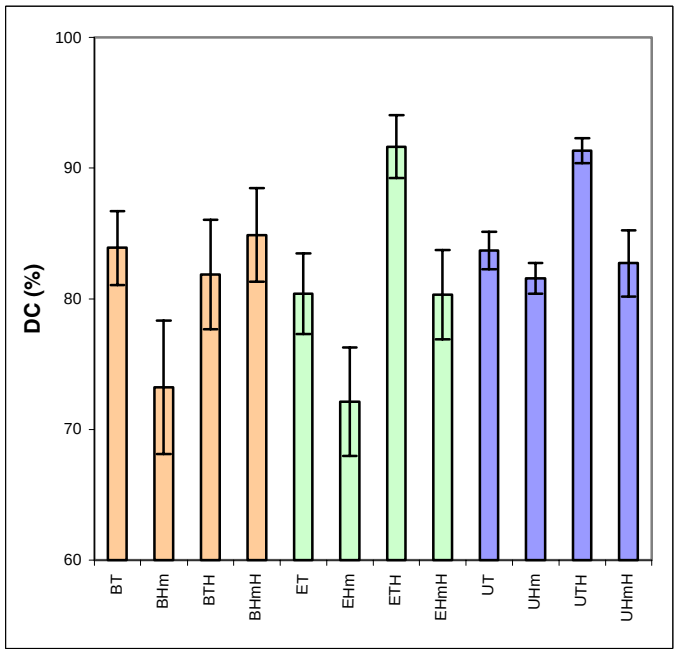

Fig. 1c. DC of Si-ACP filled composites.

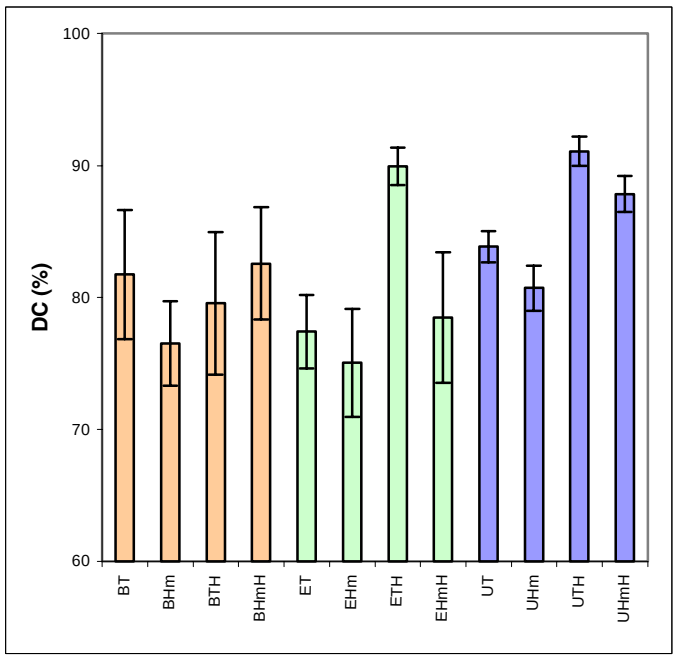

Fig. 1d. DC of Zr-ACP filled composites.

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