

Effect of Resin Composition on the Remineralizing Ability of Amorphous Calcium Phosphate-based Polymeric Composites

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The relatively high solubility of amorphous calcium phosphate (ACP) and its rapid conversion into hydroxyapatite (HAP) in aqueous environments make ACP suitable as a potential mineralizing agent. We have recently shown that when ACP is compounded with appropriate polymerizable dental resins, bioactive composites are formed with the potential for preventing tooth demineralization and actively promoting remineralization.

The objective of this study was to evaluate the effects of the chemical structure and compositional variations of the resins on the release of mineral (Ca^{2+} and PO_4) ions from ACP-filled composites, i.e. their remineralization potential.

Five photoactivated resins, designated BTHZ, TP, U0H, U66H and U132H (Table 1), were formulated from the following monomers: 2,2-bis[p-(2'-hydroxy-3'-methacryloxypropoxy)phenyl] propane (Bis-GMA), 2-hydroxyethyl methacrylate (HEMA), pyromellitic glycerol dimethacrylate (PMGDMA), triethylene glycol dimethacrylate (TEGDMA), a urethane dimethacrylate (UDMA) and zirconyl methacrylate (ZrMA).

Table 1. Composition of resins (mass fraction, %).

Monomer	BTHZ	TP	U0H	U66H	U132H
BisGMA	35.1	-	-	-	-
TEGDMA	35.1	48.7	-	-	-
HEMA	28.0	-	-	6.6	13.2
PMGDMA	-	48.7	-	-	-
UDMA	-	-	99.0	92.4	85.8
ZrMA	0.8	-	-	-	-

Composite pastes were made up of mass fraction of 40 % of either unhybridized, P_2O_7 -stabilized ACP (Pyro-ACP), silica- or zirconia-hybridized ACP (TEOS-ACP and Zr-ACP, respectively) with mass fraction of 60 % of each resin. Uncured pastes were examined by x-ray diffractometry (XRD) and Fourier-transform infra-red spectroscopy (FTIR) to verify that no conversion of the ACP filler to HAP occurred at this stage. Composite disks were prepared in teflon molds by visible light photocuring. The remineralizing ability of the composites was tested by immersing individual disk specimens in buffered saline solutions (pH=7.40, ionic strength = 0.13 mol/L, 37°C, continuous magnetic stirring) for at least 300 hours (3 independent runs in each experimental group). Aliquots were taken at the predetermined time intervals, filtered, and the filtrates analyzed for their Ca^{2+} and PO_4 contents using atomic spectroscopy and UV/VIS spectrophotometry, respectively. The thermodynamic stability of immersion solutions was calculated as their supersaturation relative to stoichiometric HAP and

expressed as the Gibbs free energy, ΔG° . Upon completion of the immersion tests, the disks were removed, dried and evaluated for the extent of ACP to HAP conversion that occurred during soaking (XRD and FTIR analysis). Experimental data were analyzed by multifactorial ANOVA ($\alpha=0.05$). To determine significant differences between specific groups, appropriate multiple comparison tests were performed.

All the composites were capable of releasing mineral ions at levels considerably above the minimum necessary for remineralization. Average ΔG° values \pm SD of the immersion solutions containing maximum levels of Ca^{2+} and PO_4 ions released from different ACP composites are given in Table 2 (a more negative ΔG° value represents a solution more supersaturated with respect to stoichiometric HAP).

Table 2. Remineralization potential of ACP composites expressed as ΔG° (kJ/mole).

	Pyro-ACP	TEOS-ACP	Zr-ACP
BTHZ	-4.88 \pm 0.22	-5.00 \pm 0.20	-5.02 \pm 0.18
TP	-4.42 \pm 0.11	-4.28 \pm 0.10	-4.33 \pm 0.13
U0H	-4.17 \pm 0.11	-6.01 \pm 0.18	-5.53 \pm 0.19
U66H	-3.95 \pm 0.11	-5.96 \pm 0.18	-6.12 \pm 0.10
U132H	-4.90 \pm 0.17	-6.62 \pm 0.19	-5.92 \pm 0.14

Elevated Ca^{2+} and PO_4 ion concentrations were sustained in all BTHZ and UH resins. However, over time TP composites failed to maintain a favorable remineralization potential due to the resin retention of released Ca^{2+} via ion binding by carboxylic acid groups of PMGDMA. Remineralizing ability of Pyro-ACP composites ranked (BTHZ, U132H) >TP> (U0H, U66H). Composites based on the TEOS- or Zr-ACP, and U0H, U66H or U132H had significantly higher ($p \leq 0.0013$) remineralization potential compared to the similarly prepared Pyro-ACP UH composites. Hybridization of the fillers had no effect on the ion release from BTHZ composites. However, internal conversion of ACP to HAP was significantly reduced or almost completely inhibited in the case of BTHZ and UH/ hybridized ACP composites.

The most probable mechanism by which hydrophilic HEMA-enriched composites increased internal ion saturation was by allowing the uptake of more matrix water and/or better accessibility of the ACP to the water already entrained. In addition to the hydrophilicity of the matrix, crosslink density may effect ion release. The elevated ion-release observed with hybridized ACP-U0H, U66H, or U132H composites was probably due to the enhanced area of contact between the hybrid ACP particulates and UDMA-based resins.

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