

Effect of Surfactants on Physicochemical Properties of Amorphous Calcium Phosphate Filled Composites

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Statement of Purpose: Our recent research on amorphous calcium phosphate (ACP) dental materials has resulted in biocompatible composites with high remineralizing ability and moderate mechanical strength^{1,2}. However, as a result of the uncontrolled agglomeration of ACP fillers within resin matrices, these bioactive composites have diminished strength and durability. In this study, we assess the role of non-ionic and anionic surfactants on particle size distribution, compositional and structural properties of ACP fillers, with special emphasis on the mechanical stability of the composites made with such fillers. It is anticipated that surfactants, introduced *ab initio* during the synthesis may be adsorbed on the ACP surface and reduce the ACP's agglomeration, leading to improved dispersion of this filler in the resin. Additionally, surfactants may affect the water content of zirconia (Zr)-hybridized ACP² (used as control) and affect the mechanical strength of composites.

Methods: ACP was synthesized as previously described². A 0.10 % by mass of surfactant (Table 1) was added to either Ca component (non-ionic surfactants) or PO₄ component (anionic surfactant) prior to precipitation. Chosen surfactant level corresponds to the upper limit of the reported effective range for fluoro-surfactants in adhesive applications. ACP fillers were characterized by X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), particle size distribution (PSD) analysis and thermo-gravimetric analysis (TGA).

Table 1. Surfactants utilized in the study.

Surfactant	Empirical formula
<i>Non-ionic:</i>	
Triton 100	C ₁₄ H ₂₂ O(C ₂ H ₄ O) ₁₀
Tween 80	C ₂₄ H ₄₄ O ₆ (C ₂ H ₄ O) ₂₀
FSN	F(C ₂ F ₄) _x (C ₂ H ₄ O) _{1+y} H; x=1-9, y=0-25
<i>Anionic:</i>	
FSP	F(C ₂ F ₄) _x (C ₂ H ₄ O) _y HP(O)(ONH ₄) _z ; x=1-7, y+z=3

The experimental resin, photoactivated with camphorquinone and ethyl-(4-N,N-dimethylamino benzoate, was formulated from the commercially available dental monomers 2,2-bis[p-(2'-hydroxy-3'-methacryloxypropoxy)phenyl]propane (Bis-GMA) and diluent monomer triethylene glycol dimethacrylate (TEGDMA) in 1:1 mass ratio. Biaxial flexure strength (BFS) of composite disk specimens (resin:filler=3:2 by mass) was determined by using a computer-controlled universal testing machine and calculated according to the ASTM specification.³ Experimental data were analyzed by ANOVA ($\alpha = 0.05$) and by all pair-wise multiple comparisons (t-test).

Results/Discussion: Solids precipitated in the presence of surfactants retained their amorphous nature. XRD showed no discrete peaks but rather two diffuse broad bands. The corresponding FTIR spectra revealed PO₄ stretching and

PO₄ bending absorption peaks at (1200-900) cm⁻¹ and (630-500) cm⁻¹, respectively, typical for non-crystalline calcium phosphates. The results from PSD analysis, TGA and BFS testing are summarized in **Table 2**.

Table 2. PSD, TGA and BFS data for surfactant-ACPs compared to Zr-ACP control. Indicated are mean values with one standard deviation (SD) given in parenthesis. SD is taken as an estimate of standard uncertainty. Minimum number of repetitive experiments 3/group.

ACP type	median diameter, d _m (μm)	water content (mass %)	BFS (MPa)	
			Dry	Wet
Triton 100	8.3(1.4)	16.5(1.4)	73(6)	28(3)
Tween 80	8.9(2.1)	15.0(4.4)	76(8)	32(10)
FSN	6.5(1.2)	19.3(1.3)	58(11)	28(3)
FSP	4.1(0.4)	17.7(1.5)	60(8)	32(10)
Zr (control)	7.4(2.1)	17.3(1.6)	68(13)	65(15)

There were no significant changes in the PSD of surfactant-modified ACP fillers compared to Zr-modified ACP except for the anionic FSP, where a 45 % reduction in d_m was seen. This reduction in d_m did not improve the mechanical performance of the corresponding Bis-GMA/TEGDMA composites. The BFS of all surfactant-ACP composites decreased by 50 % or more after a month-long exposure to saline solutions. Furthermore, there was no change in the amount of water incorporated into ACP regardless of the type of the additive used during its synthesis. TGA results additionally showed that the ratio between the loosely-bound and structure-incorporated water had not been affected.

Conclusions: Introducing surfactants during the spontaneous formation of ACP from supersaturated calcium and phosphate solutions stabilized the solid phase, but had very little or no effect on the PSD or the water content of ACP. The surfactant-ACP/Bis-GMA/TEGDMA composites showed no improvement in their dry strength but showed drastic reduction in strength after prolonged aqueous exposure. Further studies are needed on surfactant treated ACPs to establish the role of surfactant structure and method of application on particle size, water content, dispersion of ACP in matrix resins, and, ultimately, clinical suitability of ACP composites.

References:

1. Skrtic *et al.*, Biomaterials 2004;25:1141-50.
2. Skrtic *et al.*, J. Res. NIST 2003;108:167-82.
3. ASTM F394-78, re-approved 1991.

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