

# Urethane Methacrylate Resin Based Amorphous Calcium Phosphate Composites

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**Introduction.** Calcium phosphates occur in normal skeletal tissues and unwanted calcification of non-mineralized tissues and synthetic materials. Crystalline hydroxyapatite (HAP) is the structural prototype of the major mineral component of teeth and bones and is also found in well-developed calcium deposits in bioprosthetic heart valves. Amorphous calcium phosphate (ACP), a postulated precursor to HAP, shows high solubility/degradability in aqueous media and liberates  $\text{Ca}^{2+}$  and  $\text{PO}_4$  ions during its transformation to HAP. These properties suggest that ACP could be a successful bioactive filler material in dental and bone substitute applications (1). This study investigates the effect of three types of matrix-forming urethane resins on the strength and ion release profiles of their ACP composites.

**Experimental Methods.** Three photoactivated resins (Table 1) were formulated from commercially available monomers: urethane dimethacrylate (UDMA), a poly-ethyleneglycol extended UDMA (PEG-U), and a UDMA/PEG-U blend. The photo-initiator system comprised camphorquinone (mass fraction of 0.2 %) and ethyl(4-dimethylaminobenzoate) (mass fraction of 0.8 %).

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

Monomer/resin	UDMA	UDMA/PEG-U	PEG-U
UDMA	99.00	74.25	-
PEG	-	24.75	99.00

Composite pastes consisted of mass fractions of 40 % zirconia-hybridized ACP with mass fractions of 60 % of each resin. Uncured pastes were examined by X-ray diffractometry and FTIR spectroscopy to verify that no conversion of the ACP filler to HAP had occurred at this stage. Composite disks (6 specimens/experimental condition) were formed in Teflon molds by visible light curing of the pastes for 2 min/side.

Biaxial flexural strength (BFS) values of the dry and wet (after 2 weeks of immersion in HEPES-buffered, pH = 7.40, saline solutions) composite disk specimens were determined by using a computer-controlled universal testing machine. BFS values were calculated according to mathematical expressions given in ref. (2) and are shown, along with their standard uncertainties, in Fig. 1.

The remineralizing potential of the composites was tested by immersing individual disk specimens in buffered saline solutions (pH = 7.4, ionic strength = 0.13 mol/L, 37°C, continuous magnetic stirring) for at least 300 h (3 independent runs in each experimental group). Aliquots taken at the predetermined time intervals were analysed for the  $\text{Ca}^{2+}$  and  $\text{PO}_4$  contents (standard uncertainties: 29.9 % and 10.9 %, respectively).

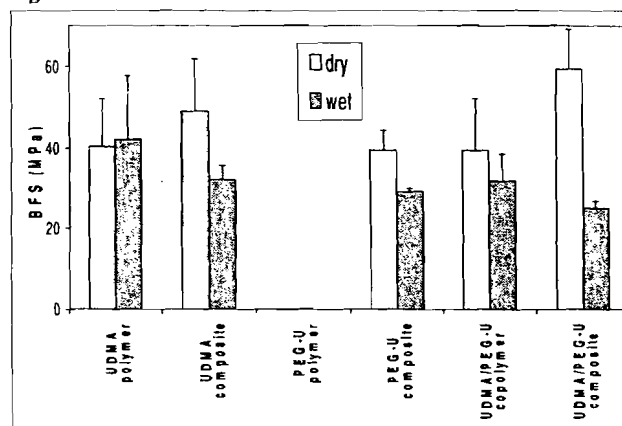
Experimental data were analysed by ANOVA ( $\alpha = 0.5$ ). Significant differences between specific groups were determined by all pair-wise multiple comparisons.

**Results and Discussion.** All of the composite samples showed a decrease in the ultimate BFS as a result of immersion in saline (Fig. 1). The unfilled PEG-U polymer was too compliant to measure by this experimental technique.

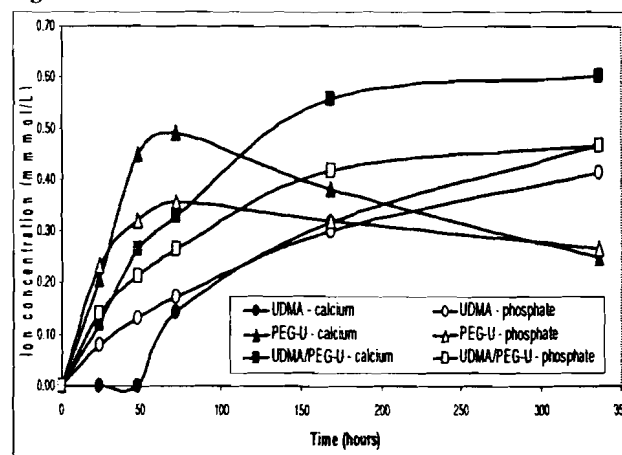
All the composites showed an initial release of mineral ions as shown in Fig. 2. The initial release of  $\text{Ca}^{2+}$  from the UDMA composite was delayed, but subsequent measurements showed a kinetic response similar to release of  $\text{PO}_4$ . The UDMA/PEG-U composite may be reaching a maximum ion release around 300 h. The PEG-U composite showed a high initial release of both  $\text{Ca}^{2+}$  and  $\text{PO}_4$  ions that attained a maximum around 72 h followed by a

decrease in ionic concentrations. It is speculated that this high initial rate of ion release in the PEG-U composite is due to the hydrophilic nature of the polymer. The increased water content in this material accelerates the internal conversion of the ACP to HAP. The subsequent decrease (after 72 h) in ion concentration is then, perhaps, due to a re-deposition of the ions onto the mineralized surface of the composite that provide nucleating sites for apatite formation. The relatively abrupt inversion in ionic concentration suggests a possible mechanism for the pathological calcification of cardiovascular tissues and implants. Further experiments are planned.

**Figure 1.** Ultimate Biaxial Flexural Stress.



**Figure 2.** Ion Release as a Function of Time.



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### References.

- (1) D. Skrtic et al., *J. Res. Natl. Inst. Stand. Technol.* 108, 2003, 167-182.
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