# Structure/Property Relationships in Urethane Dimethacrylate-based ACP Composites

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**Statement of Purpose:** Bioactive, amorphous calcium phosphate (ACP) filled urethane dimethacrylate (UDMA)-based composites, which may provide a simple model system for bone and teeth calcification, have recently been evaluated for their mechanical performance and ion release upon exposure to biological fluids[1,2]. Their properties depend on the condition of the filler/resin interface, the composition of the resin and the type of the filler phase. All resin-based composites are subject to the shortcomings of the resin matrix phase including shrinkage upon polymerization (PS), polymerization stress development (PSD) and incomplete vinyl group conversion or degree of cure (DC). Their mechanical performance is strongly dependent on matrix chemical structure and DC. Usually, a stiff polymer matrix and a high DC enhance the modulus of the material. However, high DCs also can enhance PS and PSD. This may lead to the failure of the internal (intra-composite) or the external, composite/tooth interface. Lower DCs, on the other hand, indicate the higher potential for leaching out the unreacted monomeric species from the composite (compromised biocompatibility) as well as inferior mechanical properties. In this study, the effects of two comonomers (the low molecular mass, hydrophilic 2-hydroxyethyl methacrylate (HEMA) vs. the high molecular mass, less hydrophilic, more flexible polyethyleneglycol extended UDMA (PEG-U)) on the PS, PSD and DC were assessed in UDMA/ACP composites. Additionally, dry composite specimens were evaluated for their biaxial flexure strength (BFS).

**Methods:** Zirconia-hybridized ACP (Zr-ACP) was synthesized and characterized as previously described[3]. The experimental resins, photoactivated with camphorquinone (CQ) and ethyl-(4-N, N-dimethylamino benzoate (4E), were formulated from the commercially available UDMA, PEG-U and, and (HEMA) (**Table 1**).

**Table 1**. Composition of resins# (% by mass*).

| Resin/monomer | UDMA | PEG-U | HEMA |
|---|---|---|---|
| UDMA/PEG-U | 74.25 | 24.75 | - |
| UDMA/HEMA | 92.00 | - | 7.00 |

# Photoinitiator system (% by mass) : CQ = 0.20; 4E = 0.80.
* based on equivalent molar concentration of UDMA comonomer.

BFS of dry composite (resin:filler=3:2 by mass) disk specimens (stored in air at 23 °C for 24h) was determined by using a computer-controlled universal testing machine and calculated according to the ASTM specification.[4] Near-IR was used to determine the DC of the composite specimens by monitoring changes in the 6165 $cm^{-1}$ absorption band for the vinyl group immediately after and 24 h after photo-curing at 23 °C.[5] The PS and PSD of composite resin samples were measured by a computer-controlled mercury dilatometer and a computer-interfaced tensometer, both developed by ADAF.[5, 6] Experimental data were analyzed by ANOVA ($\alpha = 0.05$) and by all pair-wise multiple comparisons (t-test).

**Results/Discussion:** Previous studies[1,2] showed that the release of Ca and $PO_4$ ions from ACP composites based on the UDMA/PEG-U was similar to that from UDMA/HEMA composites[3]. The results from this study, dealing with DC, PS, PSD and BFS, are compiled in **Table 2**. Indicated PSD values were obtained with a beam length of 12.5 cm and a beam spring constant = 3.9 N/μm.

**Table 2.** Mean values of DC, PS, PSD and the BFS of Zr-ACP UDMA/PEG-U and UDMA/HEMA composites. The standard deviation in ( ) is an estimate of the standard uncertainty. Minimum number of experiments: 3/group.

| Parameter | UDMA/ PEG-U | UDMA/ HEMA |
|---|---|---|
| DC (%) immed.<br>24 h | 74.5 (0.8)<br>79.7 (0.9) | 72.7 (0.6)<br>76.0 (0.3) |
| PS (% vol) | 4.4 (0.4) | 4.2 (0.2) |
| PSD (MPa) | 3.4 (0.1) | 4.5 (0.1) |
| BFS (MPa) | 65.4 (16.9) | 75.6 (14.3) |

Significantly higher levels of DC were attained in PEG-U containing matrix compared to the HEMA-containing matrix. PS showed no dependence on the resin composition. However, higher PSD values were obtained in HEMA-containing resin composites. The higher DC attained in UDMA/PEG-U specimens would imply that this material would have a higher PSD. The fact that the PSD is lower for the UDMA/PEG-U composition is probably due to the higher molecular mass and the more elastomeric nature of PEG-U monomer compared to HEMA. BFS values obtained with dry PEG-U composition were not statistically different from those obtained with dry HEMA composition.

**Conclusions:** Substituting PEG-U for HEMA in UDMA based ACP composites moderately improved vinyl conversion while not adversely affecting their physicochemical properties. Less polymerization stress of PEG-U formulations may result in improved clinical performance of such materials.

**References:**

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