Improved Dental Composites Utilizing Dibenzylidene Sorbitol Networks

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Summary: Dibenzylidene sorbitol (DBS) is a sugar derivative that is capable of self-organizing into a 3D nanofibrillar network at relatively low concentrations in a wide variety of organic solvents and polymer melts to induce physical gelation. This research was aimed at determining the effect of DBS networks on vinyl conversion, polymerization shrinkage, and mechanical strength of bioactive dental composites containing zirconyl-modified amorphous calcium phosphate (Zr-ACP) and a polymer matrix derived from the photopolymerization of ethoxylated bisphenol-A dimethacrylate (EBPADMA). Flexural strength was enhanced while polymerization shrinkage and its associated stress development were both significantly reduced by the incorporation of DBS into the composites, suggesting that DBS may be a useful additive for dental composites.

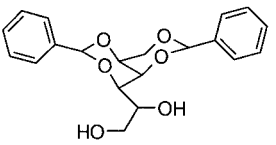
Keywords: dental composites; dental polymers; gelation; shrinkage; strength

Introduction

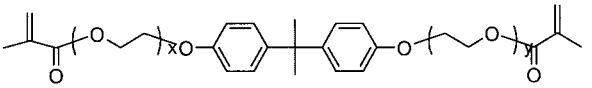
Low-molecular mass organic gelators (LMOGs), a class of organogelators, have garnered significant attention due to their ability to self-assemble and promote gelation in a variety of organic solvents and polymer melts.[1-3] Dibenzylidene sorbitol (DBS), shown in Figure 1, is a LMOG capable of inducing physical gelation in a wide variety of organic solvents and polymer melts by forming rigid three-dimensional networks.[4-16] DBS is a relatively benign material that is already in use in cosmetic applications.[17, 18] Recent efforts in this laboratory have found that DBS is capable of gelling a wide variety of dental monomers including monofunctional monomers such as methyl methacrylate, benzyl methacrylate and 2-hydroxyethyl methacrylate, as well as difunctional monomers including 2,2-bis[p-(2'-hydroxy-3'-methacryloxypropoxy) phenyl] propane (BisGMA), ethoxylated bisphenol-A dimethacrylate (EBPADMA), poly(ethylene oxide) dimethacrylate and 1,6-hexamethylene dimethacrylate. This research was aimed at determining the effect of DBS networks on vinyl conversion, polymerization shrinkage, and the mechanical strength of bioactive dental composites filled with zirconia-modified amorphous calcium phosphate (Zr-ACP) in a matrix derived from the photo-curing of an

 DOI: 10.1002/masy.200550925

EBPADMA (Figure 1), a common dental monomer that is capable of dissolving up to 10 % by mass fraction DBS.



DBS



EBPADMA (x+y ≅ 12)

Figure 1. Structures of DBS and EBPADMA.

Materials and Methods

Synthesis of Zr-ACP. Zr-ACP filler was prepared as follows: 9.51 g of sodium phosphate (GFS Chemicals, Powell, OH) and 0.61 g of sodium pyrophosphate (J.T. Baker, Phillipsburg, NJ) were dissolved with mechanical mixing in 58 mL of distilled water and 67 mL of 1 mol/L sodium hydroxide for approximately 15 min. To this solution, 21.3 g of calcium nitrate tetrahydrate (Sigma-Aldrich Corp, St. Louis, MO), dissolved in 85 mL of distilled water, and 40 mL of a 0.25 mol/L zirconyl chloride (GFS Chemicals, Powell, OH) solution were simultaneously added resulting in instant precipitation. After approximately 5 min of mixing, the precipitated Zr-ACP was washed with ammoniated water and cold acetone, vacuum-filtered, and lyophilized for 24 h according to a previously described method.[19] The amorphous state of the lyophilized Zr-ACP was verified by x-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR). The average particle size of Zr-ACP prepared by this method has been reported as (5.9 ± 0.7) μm.[20]

Sample Preparation. To prepare the organogel-modified samples, DBS (Milliken Chemicals, Spartanburg, SC) was dissolved in EBPADMA (Lot. No. 535-32, Esstech, Essington, PA) by heating the mixture in an oven at 100 °C for 2 h. While polymerization of EBPADMA can be thermally induced, FTIR spectra revealed that no polymerization occurred during this heating period. The mass average molecular mass of the EBPADMA was 888 g/mol as determined by Matrix-Assisted Laser Desorption/Ionization (MALDI)

time-of-flight mass spectrometry and the degree of ethoxylation was approximately 11.6. Upon cooling, the DBS self-assembled causing gelation of the monomer.

To activate the EBPADMA for visible light photopolymerization, 0.2 % by mass fraction of camphorquinone (Sigma-Aldrich Corp., St. Louis, MO) and 0.8 % by mass fraction of ethyl 4-N,N-dimethylaminobenzoate (Sigma-Aldrich Corp., St. Louis, MO) were added to the EBPADMA or the EBPADMA/DBS solutions (prior to gelation) and heated at 60 °C for approximately 30 min to dissolve the photoinitiators. Composite specimens containing Zr-ACP were prepared by hand-mixing the activated EBPADMA or EBPADMA/DBS gels with 30 % to 45 % by mass fraction Zr-ACP.

Three main sets of samples as well as two additional formulations were prepared and are summarized in Table 1. The first set of samples consisted of EBPADMA with 0 %, 5 % or 10 % by mass fraction DBS, the second set contained a constant filler (DBS + Zr-ACP) loading of 40 % and the third set contained a constant Zr-ACP loading of 40 %. Samples 4 and 5 had 43 % and 45 % Zr-ACP, respectively, and 5 % DBS, and were used in the shrinkage and stress measurements to isolate the effect of filler loading.

Table 1. Sample compositions in % by mass fraction; standard uncertainty is ± 0.05 %.

Sample Name	% filler in sample (DBS + Zr-ACP)	% DBS in sample	% DBS in EBPADMA	% EBPADMA in sample	% Zr-ACP in sample
1-a	0	0	0	100	0
1-b	5	5	5	95	0
1-c	10	10	10	90	0
2-a	40	0	0	60	40
2-b	40	3.1	5	60	36.9
2-c	40	6.6	10	60	33.4
3-a	40.0	0	0	60.0	40
3-b	43.0	3.0	5	57.0	40
3-c	44.8	4.8	8	55.2	40
3-d	45.9	5.9	10	54.1	40
4	45.8	2.8	5	54.2	43
5	47.7	2.7	5	52.3	45

Rheology. Rheological measurements were performed on an Advanced Rheometric Expansion System (ARES, Rheometric Scientific, Piscataway, NJ). Tests on the EBPADMA were performed using 50 mm cone and plate geometry with a cone angle of 0.04 rad. Steady rate sweeps were performed with a 300 s measurement time from 1/s to 50/s. Measurements on gelled EBPADMA specimens containing 5 % DBS were run using

25 mm parallel plate geometry. Frequency sweeps were conducted in the linear viscoelastic regime at 0.1 % strain from 0.01 rad/s to 200 rad/s to calculate the elastic modulus (G') and the viscous modulus (G").

Conversion Measurements. Vinyl group conversion was measured using mid-FTIR[21] by monitoring the reduction in the C=C vinyl band (1637 cm^{-1}) in comparison to an unchanged aromatic band (1583 cm^{-1}) used as an internal standard. A drop of the sample was spread between two KBr plates and after an initial spectrum was taken, the specimen was cured (polymerized) within the KBr plates with visible light (λ = 470 nm), 60 s per side (Triad 2000, Dentsply, York, PA). At least 3 specimens per sample were used to determine an average vinyl conversion. Measurements were taken before cure, immediately after cure, and at 24 h post-cure.

Mechanical Testing. Biaxial flexural strength (BFS) tests were performed at a crosshead speed of 0.5 mm/min using a computer-controlled universal testing machine (Instron 5500R, Instron Corp, Canton, MA) with TestWorks4 software. The BFS tests were performed on disk specimens (5 or more per sample) approximately 15 mm in diameter x 1 mm in thickness. Specimen disks were prepared by spreading the sample into circular molds that were subsequently sandwiched between two Mylar films and clamped between two glass slides. The specimens were cured 60 s per side with visible light (Triad 2000, Dentsply, York, PA) and then stored for 24 h at 37 °C before testing.

Volumetric Shrinkage. To measure volumetric shrinkage, approximately 0.9 mg to 1.0 mg of the composite specimen (3 or more specimens per sample) was placed on a 1 mm thick glass slide and positioned so that the specimen was centered inside the socket rim of a glass joint of a computer-controlled mercury dilatometer.[22] A clamp was used to ensure a tight seal between the slide and the rim, and the socket was filled with mercury. A plunger connected to a linear variable displacement transducer (LVDT) was lowered to float on the mercury meniscus. A thermistor attached to the socket of the glass joint was used to measure temperature changes while the LVDT monitored any changes in the height of the mercury. After the LVDT reached steady state, the specimen was cured for 60 s (Max Lite; Caulk/Dentsply, Milford, DE, USA) and the thermistor and LVDT measurements were taken for 60 min. The curing light was then triggered for an additional 30 s. Volumetric shrinkage corrected for temperature fluctuation was plotted as a function of time and the overall shrinkage due to curing was determined based on the mass and density of the composite specimen. Sample densities were measured by the

Archimedes principle with a microbalance equipped with a water immersion bath that allowed for specimens to be weighed both dry and submerged (Sartorious YDK01 Density Determination Kit; Sartorious AG, Goettingen, Germany).

Maximum Stress. Maximum curing stress was measured using a cantilever-beam tensometer.[23] A cylindrical specimen (minimum three specimens per sample) approximately 2.5 mm high and 6 mm in diameter was inserted between two cylindrical glass rods that had been silanized with a solution of 1 % mass fraction of 3-methacryloxypropyltrimethoxysilane in acetone. The upper rod was connected to a cantilever with an LVDT to measure height displacements resulting from curing while the lower rod was stationary. A curing light (Caulk/Dentsply, Milford, DE, USA) placed under the lower rod was triggered for 60 s to cure the specimen and the displacement of the upper rod was followed from the onset of curing to 60 min afterwards to monitor stress development.

Statistical Analyses. Data were analyzed using one-way ANOVA and the Tukey HSD test. Differences were considered significant when $P < 0.05$. In the data presentations that follow, error bars and (±) symbols indicate one standard deviation in each direction, where the standard deviation is taken as a measure of the standard uncertainty.

Results and Discussion

The EBPADMA monomer had a viscosity of (0.529 ± 0.001) Pa·s as determined through a steady rate sweep. Addition of 5 % DBS resulted in physical gelation with G' > G" and both G' and G" considered to have low dependence on frequency[24] as shown in Figure 2.

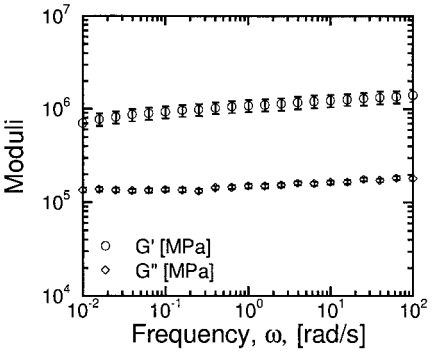


Figure 2. Frequency sweep of EBPADMA with 5 % by mass fraction DBS.

FTIR results, shown in Table 2, indicate that adding DBS to EBPADMA resulted in a statistically significant increase in vinyl group conversion of samples without Zr-ACP (samples 1-a, 1-b and 1-c). By causing physical gelation of the monomer, DBS may have induced a "Trommsdorff" effect[25, 26] where polymerization kinetics increase at high viscosities due to a reduction in chain termination accompanying the decreased mobility of the polymer radicals. Differences in vinyl conversion between samples with 5 % (1-b) and 10 % DBS (1-c), however, were insignificant. This may be due to the presence of air voids within the high-viscosity EBPADMA/DBS gels as well as reduced clarity at higher DBS loadings, both of which may inhibit photo-curing.

Table 2. Vinyl group conversion percentage of EBPADMA and EBPADMA/Zr-ACP composites 0 h post-irradiation and 24 h post-irradiation (standard deviations shown in parentheses).

Sample	0 h conversion	24 h conversion
1-a	88.9 (0.9)	90.8 (0.7)
1-b	93.0 (1.6)	95.4 (0.8)
1-c	92.4 (1.2)	94.4 (0.8)
2-a	74.6 (0.7)	77.6 (0.3)
2-b	78.2 (0.9)	80.2 (1.0)
2-c	81.7 (1.3)	83.3 (1.8)
3-a	74.6 (0.7)	77.6 (0.3)
3-b	73.2 (1.0)	76.2 (0.5)
3-d	73.2 (1.7)	76.4 (2.2)

Results for composite samples with constant filler loadings of 40 % by mass fraction (samples 2-a, 2-b and 2-c) show a statistically significant increase in conversion upon addition of DBS, but this may likely be attributed to the relative decrease in the amount of Zr-ACP as systems containing Zr-ACP had consistently lower conversions than samples without Zr-ACP. In samples with a constant Zr-ACP loading of 40 % (samples 3-a, 3-b and 3-c), there were no significant differences between samples with and without DBS. This could be due to disruption of the DBS gel structure during mixing with the Zr-ACP filler, or it may be that the high viscosity of the EBPADMA/Zr-ACP composites masks any effect of the DBS network.

Results from the mechanical testing (Table 3) reveal that the BFS of the cured EBPADMA is significantly reduced upon addition of Zr-ACP as sample 3-a had a much lower BFS than sample 1-a. This is expected due to the inherently brittle nature of the Zr-ACP and the lack of strong interactions between Zr-ACP and the EBPADMA matrix. Addition of

5 % by mass fraction DBS (sample 3-b) to the EBPADMA/Zr-ACP composites resulted in an almost 40 % increase in BFS compared to the sample without DBS (3-a). Adding 8 % or 10 % by mass fraction of DBS (3-c and 3-d, respectively), however, caused a relative decrease in the BFS. Fractographic analyses (not shown) indicate that the reduction in BFS at higher loadings is due to the nature of the air voids incorporated into the resin during mixing of the EBPADMA/DBS gels with Zr-ACP.

Table 3. Biaxial flexural strength of dry, cured EBPADMA and EBPADMA/Zr-ACP composites (standard deviations shown in parentheses).

Sample	BFS [MPa]
1-a	160 (16)
3-a	59.5 (5.7)
3-b	83.0 (3.7)
3-c	74.6 (5.1)
3-d	69.6 (4.4)

Mercury dilatometry and tensometer results for EBPADMA/Zr-ACP composites are given in Figure 3 as a function of DBS concentration calculated with respect to the composition of the entire sample. Volumetric shrinkage ranged from (3.7 ± 0.3) % for the Zr-ACP composites without DBS (sample 2-a) to (2.6 ± 0.1) % for the composites containing 3.1 % by mass fraction DBS (sample 2-b), suggesting that the DBS network may act to reduce shrinkage during polymerization.

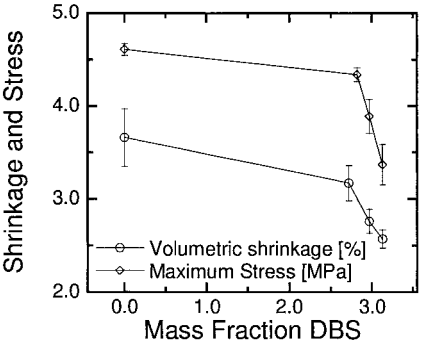


Figure 3. Volumetric shrinkage and maximum polymerization stress of EBPADMA/Zr-ACP composites containing various levels of DBS (as indicated).

Results from the stress measurements complement the shrinkage results and show that the maximum stress decreases with increasing DBS concentration. Surprisingly, the shrinkage stress and volumetric shrinkage do not appear to be affected by the total filler loading, which is highest in the samples with 2.8 % DBS (sample 4; 45.8 % filler) and 2.7 % DBS (sample 5; 47.7 % filler) and which rules out the possibility that the reductions in both shrinkage and stress are actually due to higher filler loadings.

Conclusions

The work presented here reveals that while DBS has little effect on the vinyl conversion of EBPADMA/Zr-ACP composites, it may act to increase the biaxial flexural strength and reduce polymerization shrinkage and stress. At this point it remains unclear whether the improvements are due to the DBS network or some other unknown effect of the DBS. Moreover, further studies are needed to determine if the structure of the DBS network is altered during the mixing or polymerization stages. However, these results suggest that organogelators may be useful additives for improving many of the critical properties of polymeric dental composites and related polymeric materials.

Acknowledgements

This work was supported by an interagency agreement of the National Institute of Standards and Technology with the National Institute of Dental and Craniofacial Research (NIDCR, Y1-DE-1021-04). Additional funding was received through the National Research Council Postdoctoral Associate Program. We are grateful for the gifts of EBPADMA from Esstech (Essington, PA) and DBS from Milliken Chemicals (Spartanburg, SC).

Disclaimer

Certain commercial materials and equipment are identified in this work for adequate definition of the experimental procedures. In no instance does such identification imply recommendation or endorsement by the National Institute of Standards and Technology or the American Dental Association Foundation or that the material and the equipment identified is necessarily the best available for the purpose.

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