

Supplementary Material for Biocompatible Nanocapsules for Self-Healing Dental Resins and Bone Cement

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Determination of Materials Parameters from Mechanical Tests

From the tensile tests, the displacement in the specimen was measured within the straight central portion of the constant cross section over the gauge length, L_i . The strain, ϵ_{ENGR} , of the specimen was determined by computing the change in the gauge length divided by the original length, as seen in Equation 1. The axial force that had to be applied to achieve the displacement rate varied as the test proceeded; however, this force was recorded and called the load. This force, P , was divided by the cross-sectional area, A_i , of the gauge region to obtain the stress, σ_{ENGR} , in the specimen. This is shown in Equation 2.

$$\epsilon_{ENGR} = \frac{\Delta L}{L_i} \quad \text{Equation 1}$$

$$\sigma_{ENGR} = \frac{P}{A_i} \quad \text{Equation 2}$$

Stress and strain, based on the initial (non-uniform) dimensions A_i and L_i , are known as engineering stress and strain. It was necessary to find the true stress and strain and thereby account for the changing gauge length and cross-sectional area as the test proceeded. True strain, ϵ_T , is found via Equation 3, and true stress, σ_T , is found via Equation 4.

$$\epsilon_T = \ln(1 + \epsilon_{ENGR}) \quad \text{Equation 3}$$

$$\sigma_T = \sigma_{ENGR}(1 + \epsilon_{ENGR}) \quad \text{Equation 4}$$

Stress-strain curves were made to compare the mechanical properties of the two types of resins. The stress-strain curves were made by plotting the true stress versus the true strain for each sample.

West System Epoxy Resin

The West System 105 epoxy resin is based on Bisphenol A diglycidyl ether, and it exhibits comparable properties to methacrylate-based bone cements and dental resins.

The epoxy consists of oxirane, 2,2'-[(1-methylethylidene)bis(4,1-phenyleneoxymethylene)]bis-, homopolymer (CAS #25085-99-8) at a concentration percentage between 60 to 80. The 105 epoxy resin also contains 10 to 30% benzyl alcohol (CAS #100-51-6) by concentration and 5 to 10% phenol-formaldehyde polymer glycidyl ether (CAS #28064-14-4) by concentration. The West System 209 extra slow hardener contains 30 to 60 HPR % fatty acids, C18-unsaturated, dimers, polymers with tall-oil fatty acids and triethylenetetramine (CAS #68082-29-1). It also contains 10 to 30 HPR % cyclohexanamine, 4,4'-methylenebis (CAS #1761-71-3), 10 to 30 HPR % propylene glycol diamine, 2-amino-, diether with Propylene (CAS # 9046-10-0), 7 to 30 HPR % formaldehyde, polymer with benzenamine, hydrogenated (CAS #135108-88-2), 3 to 7 HPR % formaldehyde, oligomeric reaction products with phenol and m-phenylenebis(methylamine) (CAS #57214-10-5), 1 to 5 HPR % 1,3-Benzenedimethanamine (CAS #1477-55-0), and 1 to 5 HPR % triethylenetetramine (CAS #112-24-3). 190 proof ethanol (04-355-454, Fisher) was also used to form the resins.

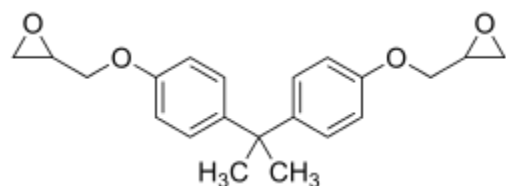


Figure S1: Bisphenol A diglycidyl ether (CAS 25085-99-8)

Impact of Nanocapsules on Mechanical Properties of the Resin

Table S1. The mechanical properties for the resin samples without capsules are shown.

	Samples with No Capsules			
	Elastic Modulus (N/mm ²)	0.2% Offset Yield Strength (N/mm ²)	Ultimate Tensile Strength (N/mm ²)	Strain to Fracture (mm/mm)

Sample 1	836.6	12.008	17.4	0.0885
Sample 2	809.8	13.2	17.9	0.0814
Sample 3	848.9	11.3	17.5	0.123
Sample 4	801.1	11.1	17.3	0.112
Sample 5	947.6	13.3	19.1	0.107
Sample 6	852.3	14.1	19.3	0.108
Sample 7	786.3	11.0	17.6	0.185
Sample 8	987.2	11.3	16.9	0.0753
Sample 9	813.6	12.5	17.1	0.108
Sample 10	742.6	12.6	17.0	0.0941
Sample 11	882.8	14.2	18.8	0.0818
Sample 12	695.8	11.7	16.5	0.125
Average	833.7 +/- 80.4	12.4 +/- 1.1	17.7 +/- 0.9	0.107 +/- 0.0294

Samples with monomer capsules

Table S2. The mechanical properties for the monomer capsule system with BPO mixed directly in the matrix

	Pre-Self-Healing			
	Elastic Modulus (N/mm ²)	0.2% Offset Yield Strength (N/mm ²)	Ultimate Tensile Strength (N/mm ²)	Strain to Fracture (mm/mm)
R1	217.2	2.8	3.6	0.0733

R2	408.8	3.3	4.3	0.168
R3	288.2	3.5	4.3	0.125
R4	322.6	3.5	4.4	0.127
Average	309.2 +/- 79.6	3.3 +/- 0.3	4.2 +/- 0.4	0.123 +/- 0.0388

R1 and R2 exhibited self-healing and were retested

Table S3. The mechanical properties for the monomer capsule system with BPO mixed into the resin post self-healing

			Post Self-Healing	
	Elastic Modulus (N/mm ²)	0.2% Offset Yield Strength (N/mm ²)	Ultimate Tensile Strength (N/mm ²)	Strain to Fracture (mm/mm)
R1	615.5	0.7	1.2	0.0118
R2	508.1	0.9	2.1	0.100
Average	561.8 +/- 75.9	0.8 +/- 0.1	1.6 +/- 0.6	0.0559 +/- 0.0624

Dual Capsule System

Table S4. The mechanical properties for the resin samples containing the dual nanocapsule system of the monomer and initiator capsules are listed.

	Pre-Self-Healing
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	Elastic Modulus (N/mm ²)	0.2% Offset Yield Strength (N/mm ²)	Ultimate Tensile Strength (N/mm ²)	Strain to Fracture (mm/mm)
R1	366.6	4.5	5.7	0.145
R2	511.4	5.3	6.6	0.100
R3	512.5	5.6	6.8	0.140
R4	506.2	5.8	7.0	0.0943
R5	505.3	5.7	6.7	0.156
R6	427.2	4.7	6.2	0.157
Average	471.5 +/- 61.0	5.3 +/- 0.5	6.5 +/- 0.5	0.132 +/- 0.0278

Table S5. The mechanical properties for the dual capsule samples after self-healing are shown.

	Post Self-Healing			
	Elastic Modulus (N/mm ²)	0.2% Offset Yield Strength (N/mm ²)	Ultimate Tensile Strength (N/mm ²)	Strain to Fracture (mm/mm)
R4	421.5	0.5	0.6	0.0341
R5	516.8	0.7	1.2	0.0812
Average	469.2 +/- 67.4	0.6 +/- 0.1	0.9 +/- 0.4	0.0576 +/- 0.0333

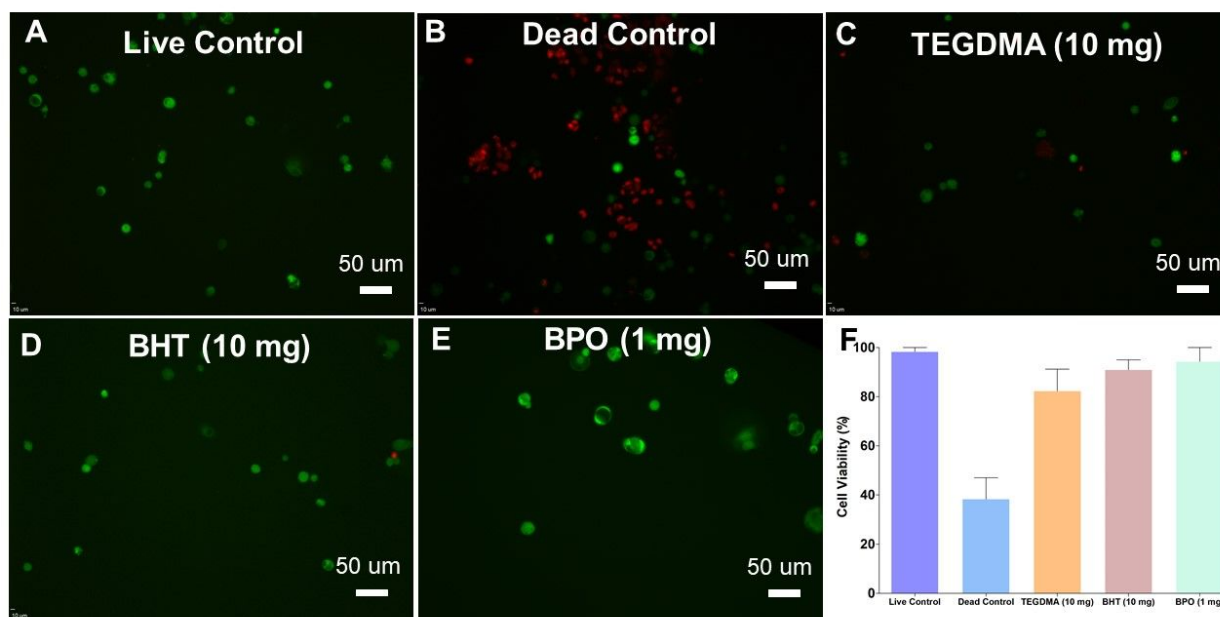


Figure S2: Results of a live/dead assay in which the cells were exposed to 1 mg or 10 mg of the various encapsulated compounds. 14,500 *CaCO2* cells were seeded per well. (A) Live control (cells cultured in media) (B) Dead control (10% ethanol) (C) 10 mg of TEGMA was added to each well. (D) 10 mg of BHT was added to each well. (E) 1 mg of BPO was added to each well. Quantification of the results of the live/dead assay can be seen in (F).