

Microencapsulation of Octylcyanoacrylate to Achieve Self-healing in PMMA Bone Cement

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Statement of Purpose: Self-healing materials are those designed to recognize, halt, and even reverse damage without requiring the application of external forces. Such materials have been investigated for civil and aerospace applications but also possess the potential for significantly extending implant lifetimes. As soon as an implant is placed in its use environment it begins an irreversible path to failure; such failure is rarely due to a single instance of damage but is more commonly seen in cyclically-loaded materials that accumulate microdamage over their usage lifetime. The self-healing approach is summarized in Figure 1. (a) A polymer matrix embedded with catalyst and encapsulated healing agent is compromised by (b) an infiltrating microcrack that exposes embedded catalyst. Propagation progresses (c), fracturing a microcapsule, and releasing the healing agent into the crack plane, which results in (d) the polymerization of the healing agent that halts crack propagation¹. One primary failure mode of cemented joint replacements results from the production of wear particles formed through micromotions around the metallic joint stem. The particles become caught in the joint space, increasing abrasion and accelerating the rate of wear, necessitating revision or replacement of the implant². Poly(methyl methacrylate), PMMA, a commonly-used bone cement, is susceptible to microcracking following sustained cyclic loading; the addition of an encapsulated healing agent would toughen the matrix and provide the means to repair microcracks, thereby reducing or halting the production of wear particles and delay implant failure. Water-reactive healing agents are desirable for the use environment and also simplify the material design; various cyanoacrylates have been studied as medical grade tissue adhesives and were selected as the encapsulated agent for these studies³. Polyurethane (PUR) is widely used in biomedical applications and was selected as the capsule material⁴. **Methods:** PUR was synthesized⁵ and interfacial polymerization used to encapsulate octylcyanoacrylate (OCA) following an oil-in-water emulsion. Interfacial polymerization of butylcyanoacrylate (BCA) was also used to encapsulate the OCA healing agent following oil-in-water emulsion. Polymerization for each procedure progressed for 1 hour at 70°C with stir speeds ranging from 500-1500rpm. Capsules were vacuum filtered and air dried for 48 hours before further characterizations were performed. Scanning electron microscopy (SEM) was used to study the size distribution of each capsule type at each stir speed. Freeze fracture techniques were used to more accurately determine average capsule thickness. Thermogravimetric analysis (TGA) was used to determine the percent fill and shelf life of the capsules; capsules were stored in both air and water at room temperature in sealed scintillation vials to determine

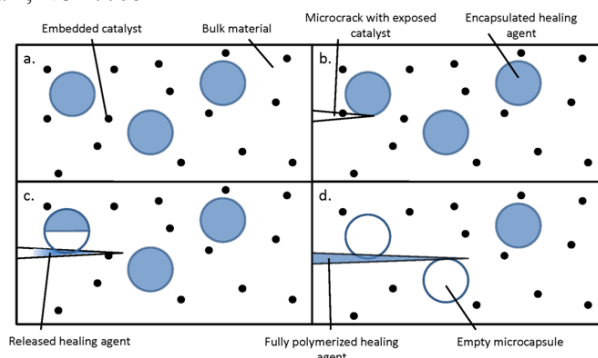


Figure 1. Self-healing via embedded catalyst and healing agent¹

capsule stability in dry and aqueous environments. Both types of capsules were analyzed 2 days and 3 months post-fabrication to study the changes in weight fractions of shell material and encapsulated healing agent over time. D&C Violet #2 dye was added at 1ppm to the OCA in order to visualize the release of healing agent from the capsules during testing.

Results: Average capsule diameters ranged from 50-500µm depending on the stir speed used during the polymerization procedure and capsule shell thickness was found to be between 1-20µm regardless of stir speed. Preliminary investigations of the durability of these microcapsules have begun; incorporation of the D&C Violet #2 will enable the visualization of capsule rupture during the mixing procedure that combines the microcapsules within the PMMA matrix.

Conclusions: Previous research has verified that this self-healing approach yields an average of 73% recovery of material strength and function⁶. Previous encapsulation procedures that employ interfacial polymerization of PUR yielded capsules with 68% incorporated healing agent and 32% shell material. However, this existing research does not employ materials that adhere to the constraints presented by biomaterials. Future studies will focus on making comparisons between the bulk characteristics of a PMMA matrix embedded with each capsule type. Interface bonding between the capsules and PMMA must be assessed and the effects of various weight percentage amounts of capsules analyzed. Composite properties will be compared to the properties of pure PMMA and the healing capabilities assessed *in vitro*.

References:

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