Microencapsulation of Concentrated Sulfuric Acid with an Epoxy Vinyl Ester Shell

Duane A Schneider[1], Dale L Huber[2], Christina Crawford[3] and Arturo Sanchez[4]

[1]*Organic Materials Department, Sandia National Laboratories, Albuquerque, NM 87185*

[2]*Center for Integrated Nanotechnologies, Sandia National Laboratories, Albuquerque, NM 87185*

[3]*Chemistry Department, Washington State University, Pullman, WA 99164*

[4] *Department of Chemistry and James Franck Institute, University of Chicago,Chicago, IL 60637*

INTRODUCTION

Microencapsulation is the process of placing a shell composed of a synthetic or biological polymer completely around another chemical for the purpose of delaying or slowing its release. Sandia National Laboratories was interested in microencapsulating concentrated sulfuric for a specific application. Historically, acids have been encapsulated many times using various techniques. However, the encapsulation of mineral acids has proven difficult due to the lack of a shell material robust enough to prevent premature leakage of the capsule. Using the Polymer-Polymer Incompatibility (PPI) technique[1], we screened a variety of shell materials and found our best results were with Derakane® 411-350, an epoxy vinyl ester resin (EVER)[(2,3)] polymer.

EXPERIMENTAL

Reagents used. Derakane® 411-350 EVER polymer was supplied by Dow Chemical Company (Midland, MI) and Ashland Inc. (Covington, KY). Dicholoromethane, toluene, HPLC-grade heptane and all acids listed below were purchased from Fisher Scientific (Waltham, MS). 50cst silicone oil was purchased from Brookfield Engineering (Middleboro, MA). N,N-dimethylaniline (DMA) and dibenzoylperoxide (DBP) were purchased from Acros Organics (Geel, Belgium). 37% v/v sulfuric acid solution was purchased from LabChem Inc. (Pittsburgh, PA). All chemicals were used without further purification.

Preparation of Microcapsules. The microcapsules were prepared using a PPI method. 0.6g of the EVER was first dissolved in 12 mLs of dichloromethane. 0.6g of 37% (v/v) sulfuric acid solution was added dropwise to the solution and stirred for 15 minutes at 1000rpm. After 15 minutes, 6 mLs of 50 cst silicone oil were added to the solution. A UV lamp, which had been warming up for 15 minutes, was then directed onto the solution to begin curing the EVER. The solution was allowed to stir for another 15 minutes and then 0.01g of DBP was added to the solution, delivered in 1 mL of heptane added dropwise to the solution. 10 µL of DMA were then added to supplement the DBP and UV light's curing of the polymer. The solution was allowed to stir again for 15-20 minutes. Meanwhile, a 1L PTFE beaker containing 900 mLs of heptane in an ice bath was set underneath a mechanical and programmable stirring apparatus with a Teflon stir blade. The mechanical stirrer was set at 350 rpm. The microcapsule solution was added dropwise to the heptane. The UV lamp was trained on the heptane solution and left to stir for 30 minutes. The microcapsules were then harvested by vacuum filtration.

MICROCAPSULE CHARACTERIZATION

The 37%(v/v) sulfuric acid EVER microcapsules were evaluated for their acid-containing properties by storing the microcapsules and then mechanically rupturing them to determine if the microcapsules still contained the acidic solution. The microcapsules were stored for six months then placed onto pH indicator strips and mechanically ruptured to release the acid cores (see figures 1, 2 and 3).

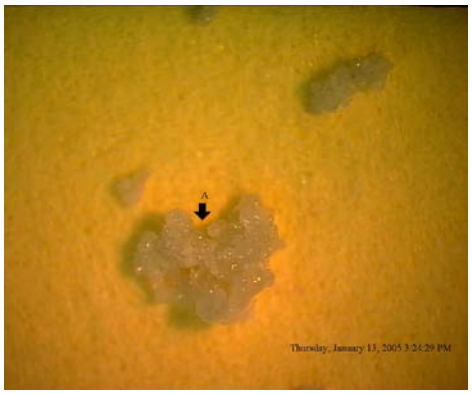

Figure 1. Digital Micrograph of Sulfuric Acid-filled Microcapsules on top of pH Paper *before* Mechanical Rupture

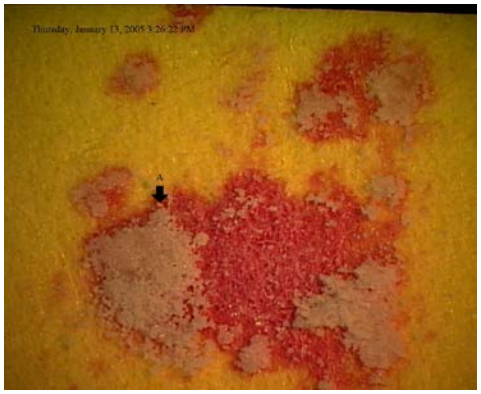

Figure 2. Digital Micrograph of Sulfuric Acid-filled Microcapsules on top of pH Paper *after* Mechanical Rupture

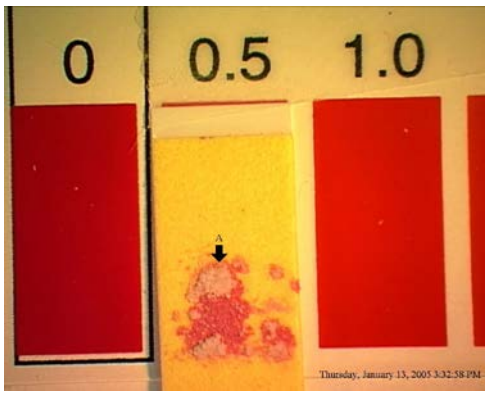

Figure 3. Digital micrograph of the same sulfuric acid-filled microcapsules shown in figure 2, comparing the corresponding color change to a pH unit

Figure 4 shows a scanning electron micrograph (SEM) of an individual 37% (v/v) sulfuric acid microcapsule before mechanical rupture. Figure 5 shows an SEM of a 37% (v/v) sulfuric acid microcapsule after mechanical rupture by fine-point tweezers. The polymeric shell has shattered, as expected for a glassy polymer.

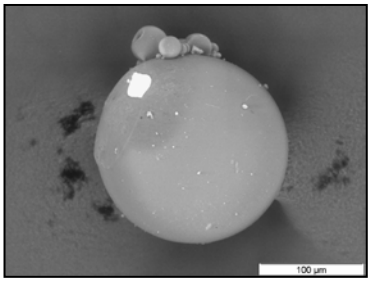

Figure 4. SEM micrograph of an individual sulfuric acid microcapsule

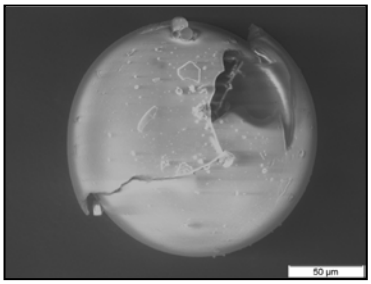

Figure 5. SEM micrograph of a mechanically ruptured sulfuric acid microcapsule

MICROCAPSULE SIZE

Individual microcapsules created by our process have an average size of about 60 micrometers and a broad, log-normal distribution as shown in figure 6. The microcapsules are generally spherical in shape but tend to aggregate, as is typical for the PPI process. These microcapsules are usually light tan in color (see figure 6).

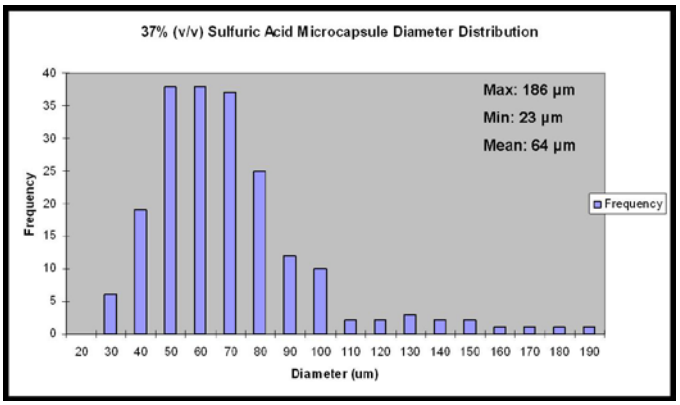

Figure 6. Histogram of microcapsule sizes as determined through image analysis of digital micrographs.

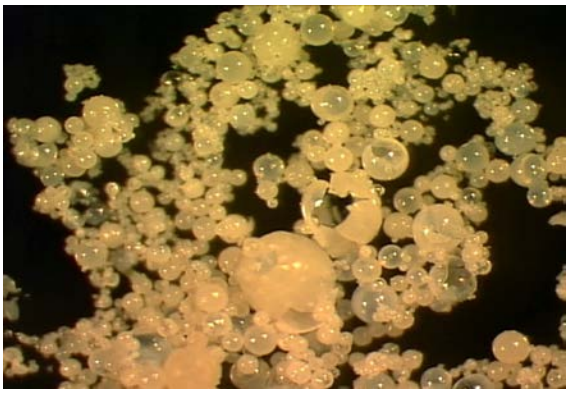

Figure 7. Digital micrograph of sulfuric acid microcapsules created using our process

CONCLUSION

The EVER shell material with mineral acid cores having concentrations up to 37% (v/v) produces microcapsules that are highly effective in storing mineral acids for extended periods of time, then quickly and safely delivering the mineral acid.

ACKNOWLEDGMENTS

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

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