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Cross-sectional analysis of hollow latex particles by focused ion beam–scanning electron microscopy

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Synthesis of hollow latex particles has been a field of extensive research and development during the past 25 years. During this time, several techniques for producing latex particles with a large central void have been developed and are reviewed in a paper by McDonald and Devon [1]. There are a number of commercial applications where hollow latex offers an alternative to solid particles. Some examples of these applications include: architectural coatings, paper coatings, low-density polymer toughening agents, micro-encapsulation for controlled polymerization and controlled release processes [1–4]. In conjunction with the development of advanced synthetic techniques there has been substantial work to characterize hollow latex particles, specifically in the field of microscopy. Scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM) techniques have all been reported in previous work for characterization of hollow latex particles [1,2,4–8]. Barner et al. [9] has discussed using a focused ion beam (FIB) for cross-sectional analysis of core-shell microspheres; however, these were solid core particles. This communication describes using a FIB to prepare cross-sections of hollow latex particles for SEM imaging in a dual beam FIB-SEM instrument. This method provides a rapid, site-specific sample preparation and characterization in one piece of equipment. The SEM and FIB have resolving power on the order of 1 and 10 nm, respectively, and the FIB can reasonably cross-section particles as small as 50 nm in diameter. Preparing samples for SEM imaging and microanalysis by FIB has been described at length in previous publications [10,11]; however, most FIB sample preparation work involves inorganic or mostly inorganic types of samples. A few papers have been published describing FIB sample preparation of polymers for SEM and TEM; again, most of these involve thin polymer films on an inorganic substrate [12–15]. To the best of the authors' knowledge this is the first paper describing hollow, organic particles that have been cross-sectioned with a FIB for electron microscope imaging.

Fig. 1 shows three variations of core-shell latex particles cross-sectioned with a FIB. The first image shows a solid particle and the subsequent images show particles with a small and large central void, respectively. Fig. 2 shows higher magnification SEM images of hollow latex particles allowing one to examine the internal polymer in more detail. Cross-sectioning particles with various core-shell structures to reveal the internal polymer material provides useful morphological data to help with interpretation of performance results such as mechanical properties. There are artifacts introduced during the FIB milling process that should be considered when examining the SEM images. The FIB implants a small amount of gallium during milling and some sputtered material may be redeposited on the interior of the particle making compositional analysis nearly impossible. Additionally the FIB may slightly heat the particles, especially in the shell, which can cause softening and subsequent relaxation of the particle shell resulting in a slightly oval-shaped particle after cross-sectioning. The shell thickness and internal polymer morphology are still useful information regardless of the artifacts introduced by the FIB.

Hollow particles are known to collapse under certain conditions and the FIB-SEM may provide valuable insight into the mechanism of collapse. Fig. 3 shows an SEM image of some collapsed particles and a FIB slice through the back side (non-collapsed region, as indicated in Fig. 3) of a collapsed particle revealing the internal structure of the collapsed shell. These data allow one to determine, for example, if the shell is too thin to withstand collapse under the specific conditions, thus enabling researchers to quickly screen candidate materials during development.

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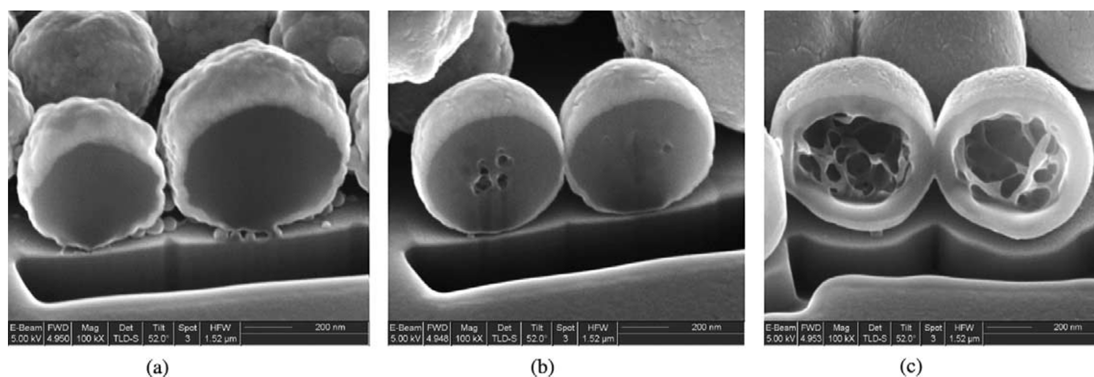

Fig. 1. (a) Solid core with shell latex particles, (b) hollow latex particles with a small central void and (c) set of particles with large central voids and thin shell material.

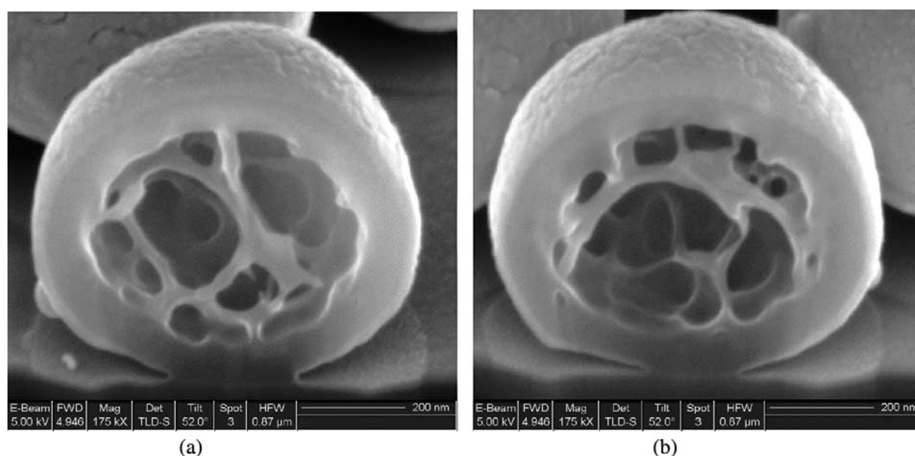

Fig. 2. High resolution SEM images of internal polymer remaining inside hollow latex particles.

The FIB-SEM provides rapid, site specific cross-sectioning that preserves the internal morphology of the hollow latex particles. This characterization tool improves our understanding of the structure–property relationships in hollow organic particles and improves the rate of introduction of new technology into the marketplace.

1. Experimental methods

A small drop of dilute latex in deionized water was placed on a clean silicon wafer and allowed to dry at room temperature under nitrogen. The dried sample was coated with approximately 40 nm of chromium using a Denton Hi-Res 100 sputter

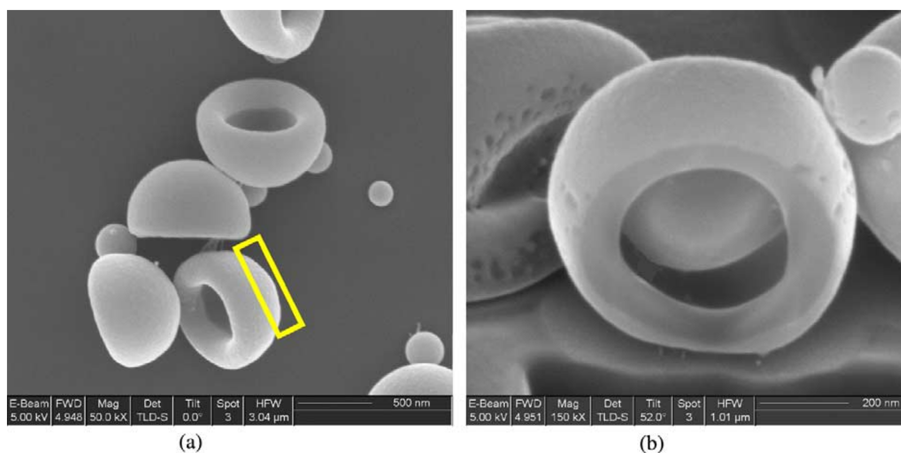

Fig. 3. (a) SEM images of collapsed particles. The yellow box indicates the 'back side' or non-collapsed region of the particle that was milled way with the FIB to expose the collapsed region. The particle shown in the image would be rotated 90° and tilted 45–55° for SEM imaging of the internal structure. (b) SEM image of a collapsed particle after a small slice has been made with the FIB to expose the internal face of the collapsed surface. (For interpretation of the reference to colour in this legend, the reader is referred to the web version of this article.)

coater. An FEI Strata DB235 FIB-SEM was used for cross-sectioning and imaging. FIB cross-sectioning was done using a nominal 30pA aperture with actual ion beam current of 27pA. A 'clean-up' cut box was used to make the cross-section through the particles using a 1.0 μs dwell time and 50% beam overlap. The dimensions of individual FIB cuts were determined by the size of the particle(s) to be cross-sectioned. The range of the (x and y) dimensions varied from 200 to 5 μm. The z-dimension (parallel to the direction of the ion beam) was set slightly smaller than the diameter of the particle due to the fact that milling on the edge of a sample results in a 2–5× increase in sputter rate. Redeposition of sputtered material on the inside of the particle is minimized by using as small of a z-dimension as possible. The time to cut through a particle was between 5 and 15 seconds. SEM imaging was performed using a 5 keV electron beam energy, 50 μm objective aperture and a working distance of approximately 5 mm. The SEM was operated in ultra-high resolution (UHR) mode, with the immersion lens system activated, using the through lens detector (TLD) operated in secondary electron collection mode.

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