Direct Imaging of the Dynamics of Solid Particulate Flow in Polymer Matrices by In-Situ Transmission Electron Microscopy

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Many of the materials used in products of interest to industrial partners of the CHEM IUCRC correspond to rigid solid particles embedded in a soft polymer matrix. Specific examples include rubber tires, paints, polymer composites, and cosmetics. Understanding the macroscopic properties of these materials requires more detailed information about the structure of these components during processing and after solidification [1]. Many fundamental questions remain about mechanism of particle motion (tumbling, rolling), shear-induced alignment, and aggregation.

X-ray and neutron scattering, rheology, and modeling have all provided important insights about the behavior of multiphase, particulate-filled materials. However there remains a need to acquire high resolution, local information about these compounds at the length scales necessary to image the individual particles during the process of flow itself. Transmission Electron Microscopy (TEM) provides high resolution capabilites that enable imaging of solids at the sub-atomic scale, with state-of-the-art instruments now capable of resolving features 0.1 nm in size. Systematic studies of particulate flow in viscous polymer matrices have been difficult, however, because the instruments use high energy electron beams (100-300 kV), and require ultrathin samples with precise control of the flow geometry.

The Martin research group, since 2009 at the University of Delaware and from 1990-2009 at the University of Michigan, has developed reliable methods for the low dose high resolution imaging of a wide variety of polymers and organic molecular solids [2][3][4]. In the past, these methods have been restricted only to solid, ultrathin films. Most recently, we have focused on in-situ techniques that have enabled the direct TEM imaging of the electrochemical polymerization of conjugated polythiophenes [5]. These experiments have revealed the oxidative polymerization of thiophene monomers from a clear, isotropic monomer solution to a dark, solid polythiophene film. We have directly imaged the nucleation and growth of thiophene oligomers and the transition to solid polythiophene films, in process obtaining unprecedented, novel insights about the mechanisms and dynamics of the viscoelastic intermediate states that mediate this phase transition.

These experiments have required the use of specially designed sample holders that are now commercially available from several vendors including ProtoChips, Hummingbird, and DENS Solutions (Figure 1). These holders now make it possible to image samples in the liquid state by creating a thin sandwich between a top and bottom chip having thin solid films of silicon nitride over a relatively small viewing area. We currently have two in-situ TEM ProtoChips holders in the UD microscopy suite, and recently finished an evaluation of a Hummingbird holder. We are in midst of evaluations of some DENS Solutions that are expected to have

additional capabilities, particularly better control of the flow behavior around the viewing window that would be important for these studies.

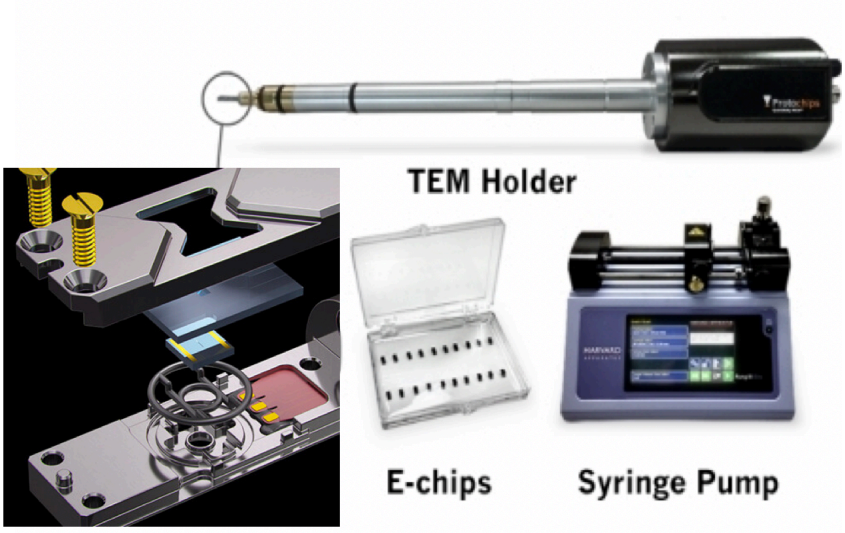

Figure 1: Schematic of a ProtoChips Poseidon Liquid Cell TEM holder.
http://www.protochips.com

This proposed project will focus on the direct imaging of solid particulate flow in a liquid polymer matrix by in-situ TEM. We will start by working with an industrial partner to identify a system of interest. We expect to examine behavior as a systematic function of particle composition, size, and shape; starting from the pure polymer control. Complimentary experiments will be done using rheology and scattering experiments with other PIs in the IUCRC depending on the level of interest and financial support. We will carefully monitor the electron beam doses to insure that radiation-induced issues are kept to a minimum, following the methods we have developed in our laboratory. Future studies could involve the change in dynamics that occurs during solidification, or the development of a thin conjugated polymer film using an electrochemical cell.

References

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