Automated Image Acquisition of Polymer Blend Morphology in an SEM

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Introduction

Modern semi-crystalline polymers based on olefin chemistry are receiving a lot of attention due to their low cost of manufacture and the ability to tailor properties by controlling polymer morphology. A common technique to visualize polymer morphology is transmission electron microscopy (TEM), with the use of appropriate contrast-enhancing heavy metal stains. One of the difficulties in obtaining a TEM image is the need to prepare an ultra-thin section. Alternative approaches that do not rely on sectioning, such as AFM and SEM imaging of a prepared block face, have shown some promise for gross morphology characterization (µm-scale) but in most cases lacked the detail that can be observed by TEM. Recent improvements in high resolution scanning electron microscopes and backscatter electron (BSE) detectors now make it possible to not only determine the gross phase morphology, but also can provide increased detail such as the lamellar structure (nm-scale) [1, 2]. The main advantage of the SEM-based technique is the ability to examine a polished surface, which requires less demanding sample preparation than producing thin sections for a TEM. BSE imaging at a relatively low accelerating voltage (~3 keV) in an SEM provides good spatial resolution while being less demanding on the microtome-polish surface finish than what it is needed for secondary electron, AFM or TEM imaging. These BSE images show high contrast and good resolution with an information content that was previously only possible in the TEM.

Sample Preparation

Polymer blend plaques were trimmed and either cryo-microtome polished at -60°C with a conventional cryo-knife or at room temperature using an oscillating diamond knife [3]. The blocks were then stained in RuO_4 vapors for 3 hours and then re-polished using a diamond knife at room temperature. Thin sections ~100 nm were collected and examined in a JEOL 1230 TEM operating at an accelerating voltage of 100 keV. The stained and re-polished block faces were examined in an FEI Nova NanoSEM 600 at 3 keV. The heavy metal staining imparted enough electrical conductivity to make a metal coating for charge compensation unnecessary. The BSE micrographs of the block face show a high contrast between the two polymer components that would lend itself to automated image analysis; the structure compares favorably to what was obtained using a TEM (Figure 1). The contrast of the SEM-BSE image was inverted in order to show the same contrast as seen in TEM images. At higher magnifications the lamellar structure of the semi-crystalline polymer can be seen clearly in the BSE micrograph and it compares favorably to what is observed in TEM images (Figure 2). Lamellar structure characterization in an SEM has been reported previously, but it has required chemical etching [4], which in practice can be an art in itself depending on the composition of the polymer.

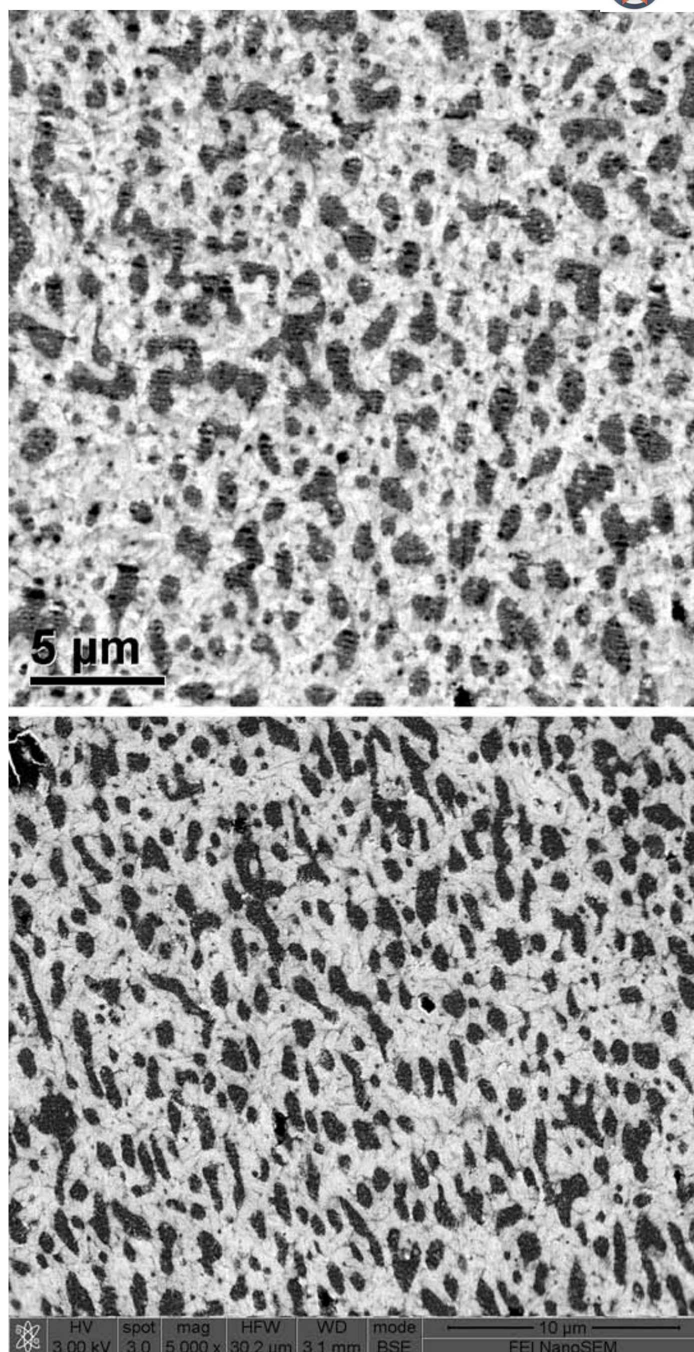

Figure 1. (a, top) Bright field TEM micrograph. The more heavily-stained phase is dark. (b, bottom) SEM-BSE micrograph. The contrast was inverted so that the heavily-stained phase is dark.

The use of a staining method along with SEM-BSE imaging has the ability to distinguish two polymer phases and inorganic additives simultaneously (Figure 3). Composites like this can be difficult to microtome thin-section for TEM as the filler particles may shatter or pluck out leaving voids or tearing of the section. In addition, the TEM grid restricts the field of view, interfering with good characterization of large or highly dispersed particles. AFM can also experience difficulty with preparation of these types of samples. The talc can appear similar to the harder polymer in phase contrast images. In addition, AFM is more sensitive to surface imperfections in the microtomed block face. There are also constraints on the field of view that is practically attainable by AFM. We have found SEM-BSE imaging to be much more forgiving on the surface

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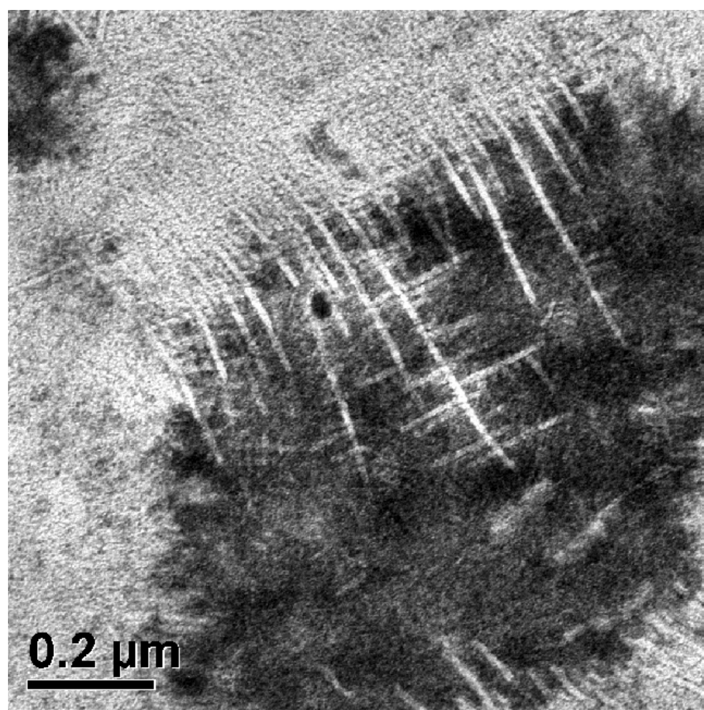

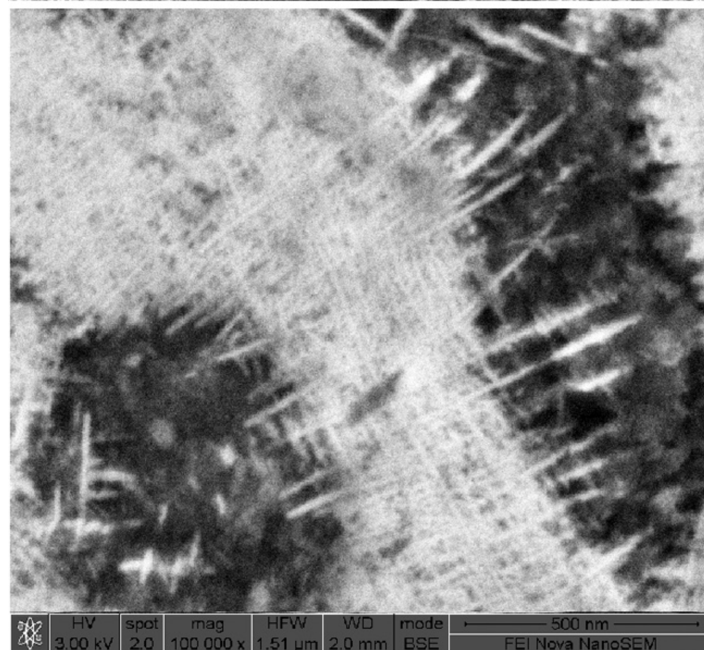

Figure 2. (a, top) Bright field TEM micrograph. The more heavily-stained phase is dark. (b, bottom) BSE SEM micrograph. The contrast was inverted so that the heavily-stained phase is dark.

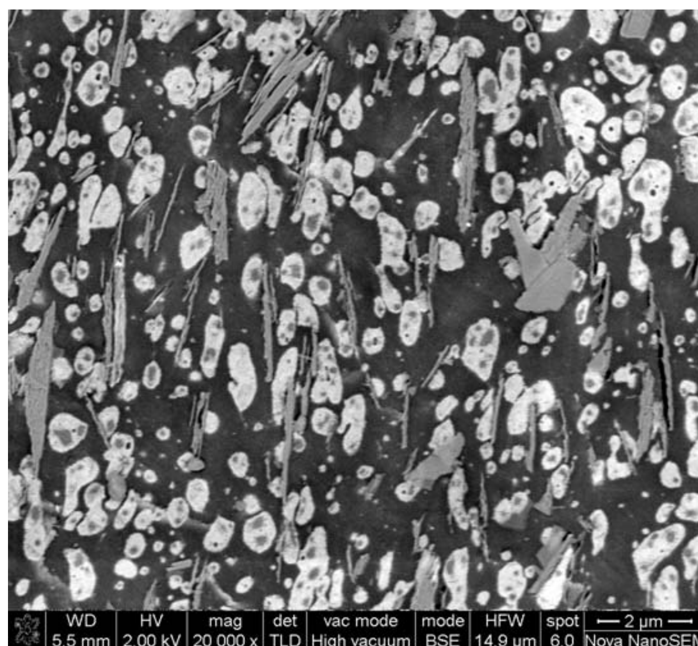

Figure 3. SEM-BSE image of stained and microtomed talc-filled polymer blend sample. The contrast was not inverted; the heavily-stained polymer is brightest, the unstained polymer darkest, and talc is intermediate in brightness.

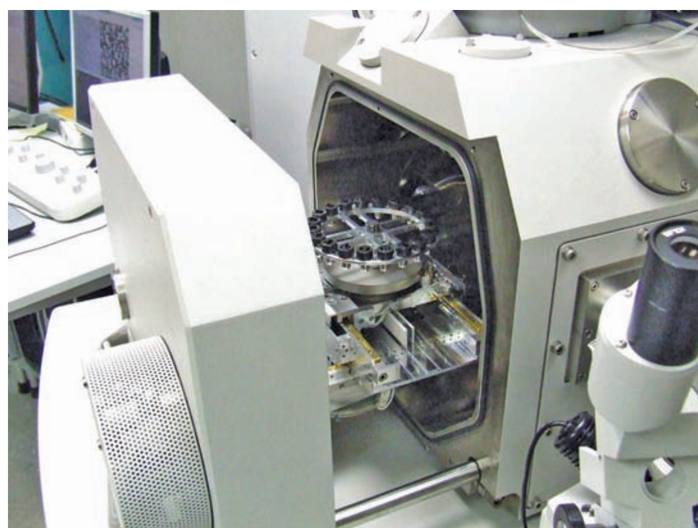

Figure 4. Multi-sample holder with 20 stained and microtomed polymer blend samples. Microtome chucks fit directly into the holder, reducing sample handling.

polish quality; the field of view is limited only by the size of the microtome-polished area.

Higher Throughput

Polymer blend morphology characterization using TEM, AFM or SEM is a relatively labor intensive analysis. As outlined above, it requires extensive sample preparation and highly experienced practitioners. Because of the high costs of the tools to perform this analysis many industrial firms, Dow included, are seeking to get better utilization of their capital investment without adding second and third shifts. Features such as automatic contrast and brightness and auto focus have been available on SEMs for a number of years. However, they are designed to work on a broad range of samples, magnifications and contrast mechanisms. Therefore ultimate performance on specific sample types may be compromised, as was the case for the magnifications desired on our polymer blend samples. Although our initial focus was on the development of a program for the imaging of polymer blend morphology that would automate the entire process from file management to image acquisition, ultimately a program that was flexible enough to work on a variety of sample types was desired.

FEI Company developed custom software for Dow to enable the automated SEM imaging of up to 20 samples in an unattended fashion. The software runs on their Nova NanoSEM 600, an immersion lens field emission gun SEM with a large sample chamber that accommodates a customized multi-sample holder (Figure 4). The software has a user-friendly interface where the number of samples to be characterized and basic microscope parameters can be selected. A number of different auto-focus routines are available, and

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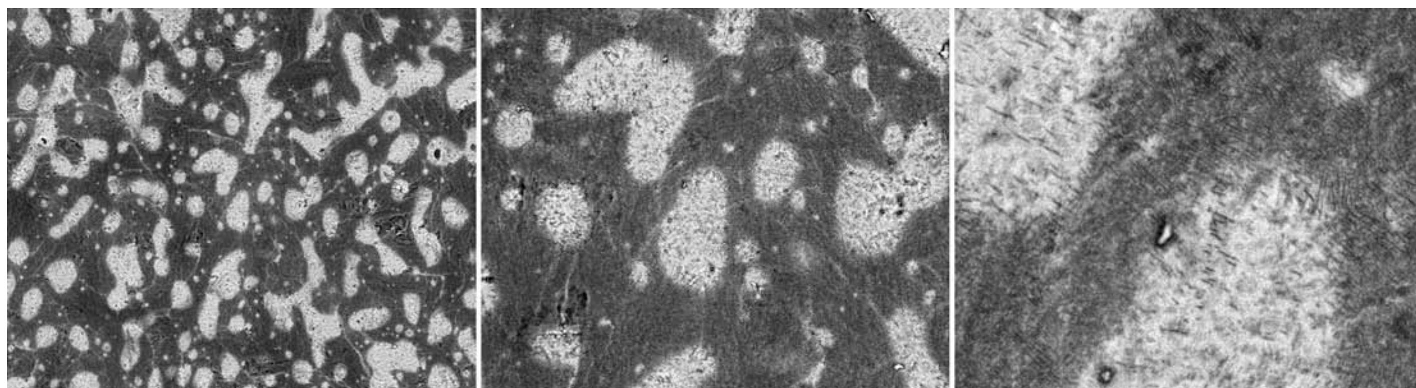

Figure 5. One of four sets of BSE micrographs on one of 20 polymer blend samples imaged with unattended automation software. (a, left) 30 µm field of view. (b, center) 10 µm. (c, right) 2 µm.

it is possible to control parameters within the routines. This allows optimization for the sample type and imaging parameters selected. It has been critically important to control auto-focus parameters to be successful for automated, high magnification, low voltage, BSE imaging of these challenging polymer blend samples. For unattended imaging the software automatically advances through all samples loaded and acquires images at multiple user-defined magnifications and locations on each sample. Currently we are acquiring images at three magnifications at each of four different locations per sample to improve sampling statistics. The program has yielded near 100% acceptable images even at the most demanding high magnification conditions needed to image the approximately 7 nm lamellar structure of semi-crystalline polymers (Figure 5).

The software also works well on less-demanding sample types. Along with polymer blend morphology, the automation program has successfully been used to image electrospun fibers and porous ceramics. ■

These and other results will be presented at Poster #178 at the Microscopy & Microanalysis 2008 conference in Albuquerque, NM. An author will be available for discussion Wednesday afternoon, August 6.

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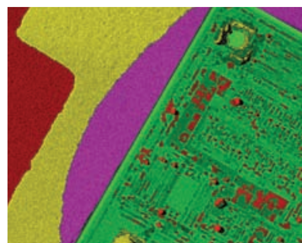

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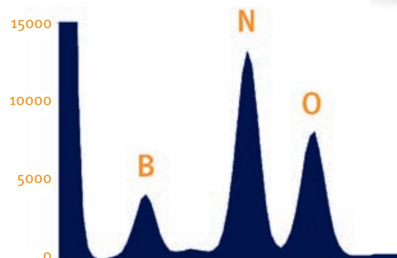

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