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New Routes to High Resolution and Automated Polymer Morphology Microscopy via Scanning Electron Microscopy

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Summary: Polymer morphologies are traditionally studied by transmission electron microscopy (TEM). With the use of appropriate contrast enhancing heavy metal stains, direct images of the morphology as well as of the lamellar structure of semi-crystalline polymers can be obtained. Despite its clear strengths, this approach faces several challenges and difficulties: the laborious nature of ultra-thin section preparation, high capital investment, and no obvious routes to high-throughput. We propose an alternative approach to cover the major morphology imaging needs based on a new generation of high resolution scanning electron microscopes (SEM) that have been developed in recent years, and that does not rely on the need for ultra-thin section preparation. The proposed approach is capable of not only determining the general phase morphology, but also to image details such as the lamellar structure with sufficient resolution. Our approach is based on the use of backscattered electron imaging at low accelerating voltages. The backscattered electron images show high contrast and information content that is comparable to TEM. The main advantage of our SEM based approach is the ability to examine a polished surface, which requires less demanding sample preparation than producing ultra-thin sections. This opens the door to automated workflows where automated imaging, substantial productivity increases and high speed characterization options can be successfully realized. The successful approach is demonstrated for various polyolefin and engineering plastics samples.

Keywords: electron microscopy; high-throughput screening; imaging; morphology; polyolefins

Introduction

The study of polymer morphology, i.e. the study of the organization and form of polymers at scales above the molecular level but below sample size, is of fundamental and applied interest. Frequently, the information obtained from morphology studies is predictive of the properties of the polymers and therefore needed to develop structure-properties-process relationships. The morphology of polymers is determined by a wide range of analytical tools including x-ray, light and neutron scattering techniques and a host of microscopy techniques including transmission and scanning electron microscopies, light microscopy, atomic force microscopy, x-ray microscopy and variants of these techniques.[1] Among the microscopy techniques, transmission electron microscopy (TEM) has been traditionally used as the main established approach to visualize polymer morphology.[2] TEM image contrast is due to electron scattering, and polymers have low atomic number and scatter electrons weakly. Therefore, it is

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necessary in most cases to stain the samples to obtain sufficient contrast for TEM imaging, particularly when visualization of different polymer phases is desired. RuO_4 or OsO_4 are typical and widely used staining agents to selectively stain polymer phases.[1,2] Additionally, ultra thin sections, less than 150 nm, need to be prepared to allow electron penetration for imaging. This is commonly accomplished through ultramicrotomy and cryoultramicrotomy either before or after staining. Once staining is achieved and sections are obtained, they are deposited on TEM grids and imaged in a TEM. Even though TEM imaging has a proven record of delivering superior polymer morphology information, it is extremely capital intensive, requires complex operation of stand-alone instrumentation, and the need to obtain ultra-thin sections. Therefore it is worthwhile to explore alternatives, particularly for cases where the ultimate high-resolution beyond 1–2 nm is not required. Until recently, alternatives were not readily available. Techniques such as atomic force microscopy (AFM) have shown to be an alternative in certain cases for polymer morphology imaging and to provide complementary information, however, it has its own limitations such as slow image acquisition, complex contrast mechanisms and inability to resolve lamellar structure on sectioned samples in most cases.

We propose an alternative approach to cover the major morphology imaging needs based on a new generation of high resolution scanning electron microscopes (SEM) that have been developed in recent years, and that do not rely on the need for ultra-thin section preparation. In addition, our approach allows automated workflows where automated imaging, substantial productivity increases and high speed characterization options can be successfully realized. Our approach is based on the use of backscattered electron (BSE) imaging of stained and polished surfaces at low accelerating voltages, an approach requiring less demanding sample preparation than producing ultra-thin sections.[3] The concept of using BSE imaging for stained and microtomed surfaces has been explored earlier.[4–6] Goizueta et al.[5,6] used BSE imaging to study several blends of RuO_4 or OsO_4 stained microtomed surfaces to obtain compositional morphology information. However, because of limitations of the BSE detector performance, the accelerating voltages required and non-optimized sample preparation, the image information remained at the level of gross morphology imaging and details at lamellae scale were not observed. In this paper we will demonstrate that recent improvements in high resolution SEMs and BSE detectors now make it possible to not only determine the gross phase morphology, but also provide increased detail such as the lamellar structure (nm-scale) with high contrast and information content that is comparable to TEM.

Experimental Part

Samples investigated were commercially available polyolefins (talc-filled thermo thermoplastic olefins, impact polypropylene copolymer, propylene-ethylene copolymer, linear low density polyethylene, high density polyethylene) and engineering plastics (acrylonitrile-butadiene-styrene, high impact polystyrene). Polymer blend plaques were trimmed and either cryo-microtome polished at $-100\,^{\circ}C$ or at room temperature with a conventional diamond trim-knife. The blocks of polyolefin samples were then stained in RuO_4 vapors overnight and then re-polished using a diamond knife at room temperature. The stained and re-polished polyolefin block faces were examined in an FEI Nova NanoSEM 600 at 3 keV without any further treatment using a solid-state backscattered electron detector under high vacuum. The sample blocks of engineering plastic were stained in an OsO_4 solution overnight and then re-polished using a diamond knife at room temperature. The stained and re-polished engineering plastic block faces were coated for few seconds with an ultra-thin Ir layer of approx. 1 nm

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thickness using an Emitech K575X coater, and then examined in an FEI Nova NanoSEM 600 at 3 keV using a solid-state backscattered electron detector under high vacuum.

Results and Discussion

Figure 1 shows scanning electron microscopy-backscattered electron (SEM-BSE) images of several polyolefin samples at low magnification where the typical goal is to visualize the gross morphology. The images were obtained on the stained and re-polished block faces without applying further treatment or coating. The heavy metal staining provided enough conductivity so that the application of a metal coating for charge compensation was unnecessary for imaging at low accelerating voltage conditions of 3 kV. The SEM-BSE images show a high contrast between the polymer components despite the low accelerating voltage. It should be noted that the contrast was inverted in order to show the same contrast as observed in TEM for comparison. The more heavily RuO_4 stained phases appear darker in the TEM images, however, brighter in the SEM-BSE images due to the higher backscattered electron yield. It should be also noted that the SEM-BSE images show basically no contribution from topography to image contrast formation because the sample surface is sufficiently flat after re-polishing.

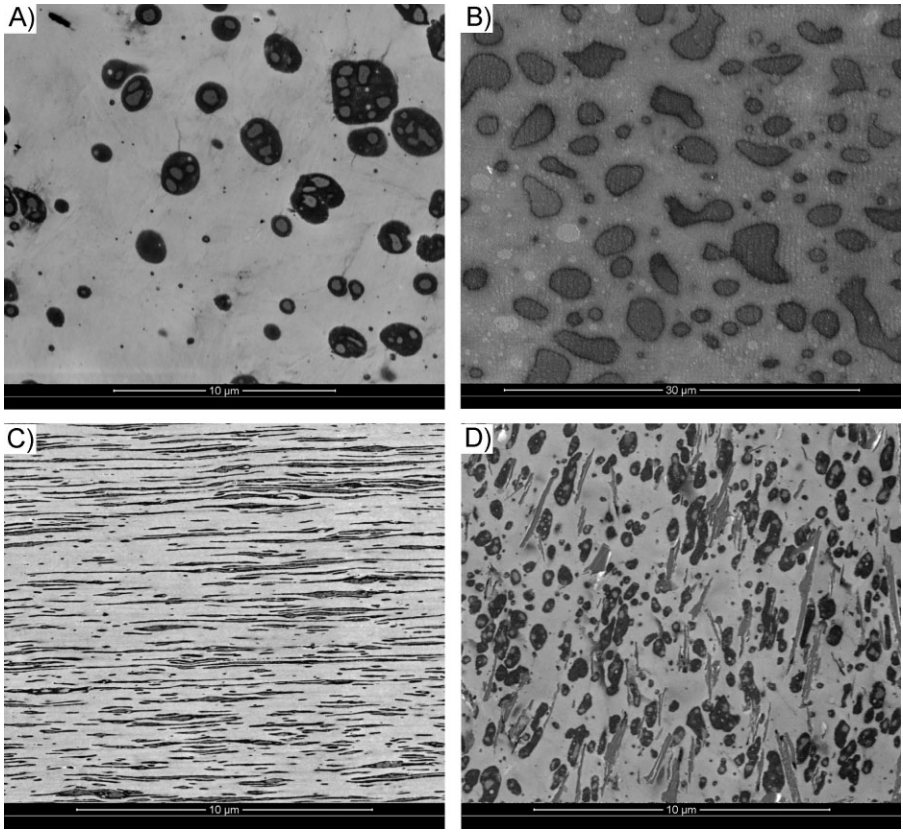

Figure 1.
Low magnification SEM-BSE images of impact polypropylene copolymer (A), blend linear low density polyethylene/propylene-ethylene copolymer (B) polypropylene copolymer film (C), and talc filled thermoplastic olefin (D) samples. Accelerating voltage was 3 kV.

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For the impact polypropylene copolymer (Figure 1A) the elastomeric domains within the matrix as well as the crystalline inclusions within the domains are resolved in high contrast which allows their full characterization in terms of nature, distribution, size and shape. For the linear low density polyethylene/propylene-ethylene copolymer blend (Figure 1B) the incompatible components as well as interfaces are clearly differentiated. The visualization of orientation and elongation of rubber domains in the polypropylene copolymer film (Figure 1C) allows for correlation to processing conditions. The use of SEM-BSE imaging can in many cases also more easily distinguish between different organic and inorganic phases present in composites samples as shown in the SEM-BSE image of a talc containing thermoplastic olefin (TPO) sample (Figure 1D). For such samples, it can be difficult to obtain good quality ultra-thin sections required for TEM as the inorganic filler particles may cause shatter or pull-out leaving voids. This is more easily avoided for the block face, and we have found SEM-BSE imaging to be much more forgiving on the surface polish quality. An important aspect is that there is contrast differentiation between the heavy metal stained elastomeric impact-modifier domains, the talc and the polypropylene matrix. This allows for excellent characterization of the dispersion, shape and size of both the dispersed impact-modifier and inorganic talc particles. Also, in contrast to TEM, there is no grid that would limit the field of view interfering with the characterization of large particles.

Many polymers are semi-crystalline in nature exhibiting nanometer-sized lamellae, and the visualization of these crystalline phases is an important aspect. Figure 2 shows high resolution SEM-BSE images of different Ru-stained, re-polished block faced polyolefins. Lamellae sized in the range of 5–10 nm in thickness are in all cases easily resolved with good contrast and information content that is comparable to TEM. Remarkable is the high information content differentiating between different crystalline lamellae types and populations within matrix, domains and interfaces. In Figure 2B for example, the different type and size of crystals within the matrix versus domain as well as the existence of an amorphous interphase is clearly distinguished. The curved shape and thickness of the lamellae can be easily estimated for the polyethylene sample shown in Figure 2D. Such high-resolution images of semi-crystalline polymers have been so far routinely obtained only by TEM. To our knowledge, this is the first time that lamellar visualization is reported based on SEM-BSE imaging of Ru-stained, block faced polymers. Previously reported lamellae visualization in an SEM and similarly for AFM was based on chemical etching, which in practice is dependent on the composition and may introduce artifacts.

A large class of polymers do not stain readily with RuO_4, and for multi-phase polymers containing unsaturated domains, staining with OsO_4 is the preferred, widely and successfully applied method. Therefore we explored the concept of SEM-BSE imaging on Os-stained, re-polished block faces. A complication encountered initially was associated with charge compensation. OsO_4 reacts selectively with the carbon-carbon double bonds in unsaturated rubber phases, and basically does not react at all with the polymer phases containing no double bonds. The conductivity of a sample after staining with OsO_4 may remain too low for charge compensation if a sample contains well dispersed, isolated rubber domains as is the case for many engineering plastics such as Acrylonitrile-Butadiene-Styrene (ABS) or High Impact Polystyrene (HIPS). Indeed, we observed charging problems when attempting to image these samples even using accelerating voltages as low as 3 kV. However, this problem could be totally avoided by applying an extremely thin metal coating using deposition times of just a few seconds.

Figure 3 shows low magnification SEM-BSE images of ABS and HIPS samples, respectively, visualizing the gross morphology. The images were obtained on the

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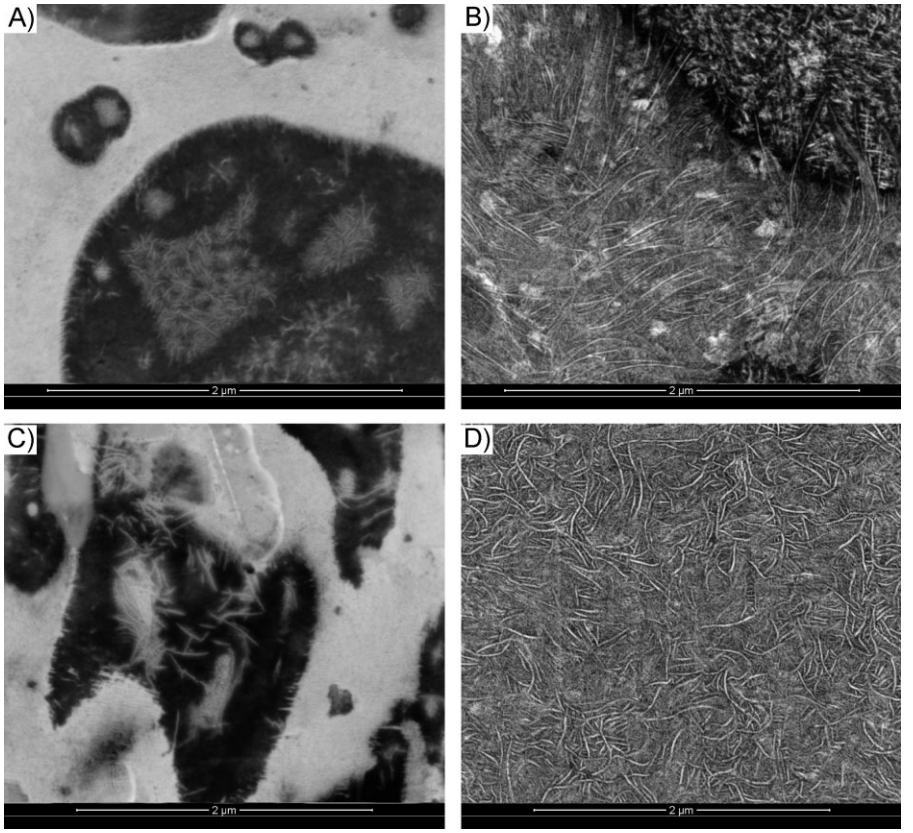

Figure 2.
High magnification SEM-BSE images of impact polypropylene copolymer (A), blend linear low density polyethylene/propylene-ethylene copolymer (B) thermoplastic olefin (C), and high density polyethylene (D) samples.

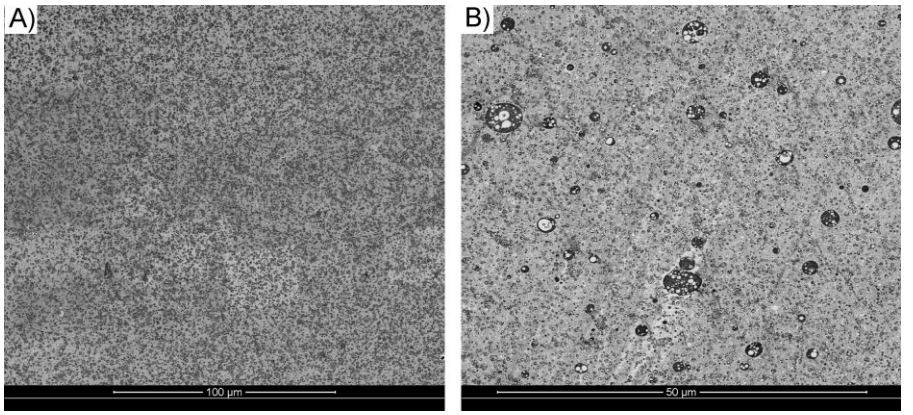

Figure 3.
Low magnification SEM-BSE images of acrylonitrile-butadiene-styrene (A) or high impact polystyrene (B).

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Os-stained, re-polished block faces after applying an approx. 1 nm thick Ir-coating. The images provided an excellent overview of the gross morphology with high contrast. An additional advantage of SEM-BSE imaging is that the field of view is limited only by the size of the microtomed-polished surface, therefore allowing much larger areas to be imaged and examined. Examination of larger imaging areas more easily allows us to address questions related to homogeneity and statistical representation of the imaged sample. For example, the image shown in Figure 3A shows the absence of larger rubber particles, while larger rubber particles are easily observed and estimated in the image shown in Figure 3B.

Similar to Ru-stained samples, high-resolution and high-contrast images can be also obtained for Os-stained, re-polished block faces. Figure 4 shows high magnification SEM-BSE images of ABS and HIPS samples, respectively. Detailed visualization of nanometer sized domains, shape and cell structure is achieved coupled with high contrast and can be used for further quantification based on image analysis methods.

The demonstrated capability of SEM-BSE imaging of stained, block faced samples opens new possibilities for automation and automated image acquisition. As outlined above, polymer microscopy and particularly TEM is very capital and labor intensive, requiring extensive sample preparation and experienced practitioners. Therefore, it is important to consider options for automation to better utilize capital investments and accelerate speed of characterization. Based on SEM-BSE imaging of black faces we propose a concept that allows for acquisition of a pre-defined number of images on a set of samples (i.e. up to 20) in an automated fashion. Based on our needs, the FEI company developed custom software enabling automated imaging of up to 20 stained, block-faced samples placed in a customized multi-sample holder (Figure 5A). The software has a user interface that allows the user to define the number of samples, number of locations per sample, magnifications and number of images per sample. Once these conditions as well as a number of basic microscope parameters have been selected, the software will locate and advance through all the samples of interest and acquire the defined number of images in a fully automated fashion using a set of auto-focus and auto-contrast routines. It has to be noted that it was critically important to optimize and to control the auto-focus and auto-contrast parameters. Auto-contrast and auto-brightness features have been available for SEMs for many years, however, they were designed for multi purpose requirements and not optimized for challenging polymer samples to be imaged in an

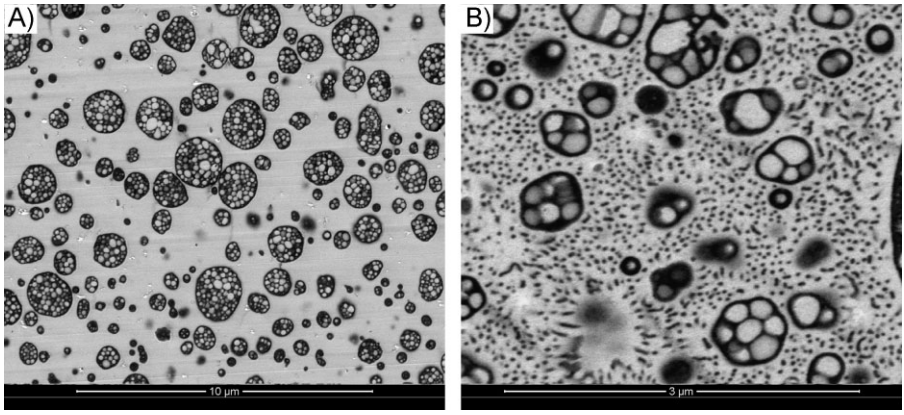

Figure 4.
High magnification SEM-BSE images of acrylonitrile-butadiene-styrene (A) or high impact polystyrene (B).

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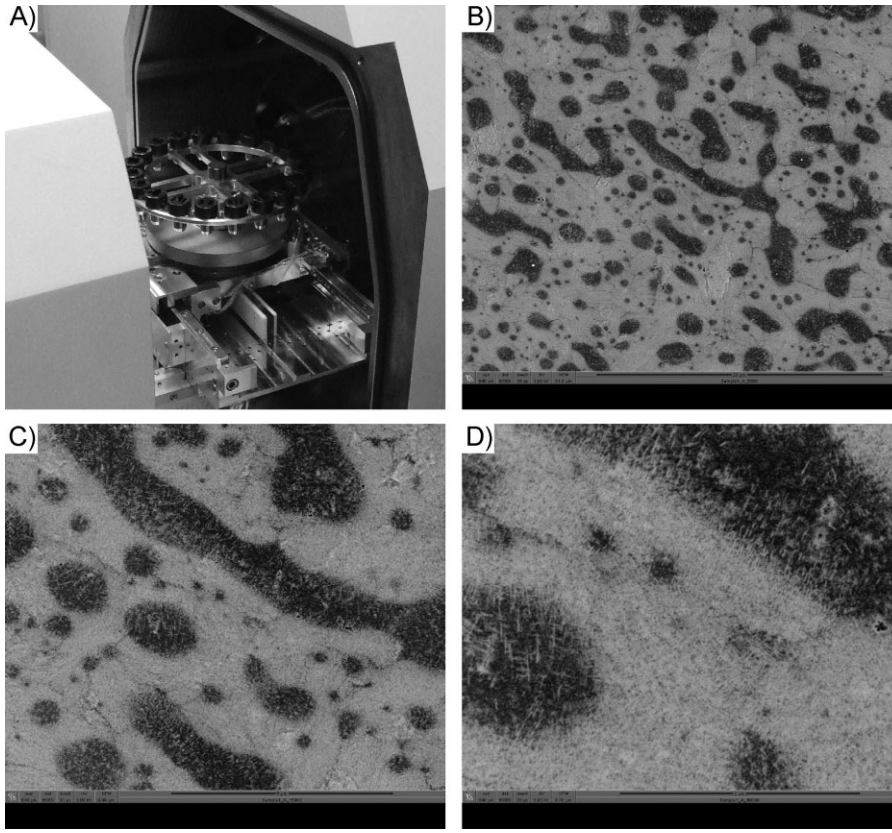

Figure 5.
Multi stage holder with 20 stained and microtomed polymer samples (A). One of four sets of SEM-BSE images on one of 20 polymer samples imaged with unattended automation software. 31 μm field of view. (B) 10 μm. (C), and 3.7 μm (D).

automated fashion at high magnifications and low accelerating voltages using SEM-BSE imaging. Figure 5 shows images of various magnifications that were acquired in a fully automated fashion.

The program has yielded almost 100% acceptable images, and the images shown in Figure 5 are representative for one of four sets of SEM-BSE images on one of 20 samples imaged (per sample four locations were examined, per location images at three magnifications were acquired, resulting in $3 \times 4 \times 20 = 240$ images in total). As can be seen, even the highly demanding imaging at high magnification to visualize lamellar structures was successfully accomplished in an automated fashion. It should be noted, that the next step of the automation approach should go beyond imaging and also address and accommodate automated sample preparation and post-processing/post-analysis of images to reach its full potential.

Conclusion

It has been shown that the morphology of a large class of polyolefin materials and engineering plastics can be successfully studied through imaging of stained, microtome polished block faces using backscattered electrons at low accelerating voltages. High contrast and high resolution images have been obtained revealing details down to the lamellar level that have so far only been routinely visualized by TEM. Further, opportunities for automated workflows

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resulting in automated imaging, substantial productivity increases and high speed characterization have been successfully demonstrated.

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