

# Morphology Characterization of High-Impact Resistant Polypropylene Using AFM and SALS

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**ABSTRACT:** Atomic force microscopy and small angle light scattering have been used to characterize the morphology of high-impact polypropylene. Because of sample preparation requirements, both techniques are relatively simple compared with conventional electron microscopy approaches. Using atomic force microscopy the spatial distribution of the impact-modifying ethylene-propylene rubber (EPR) domains could be readily identified whereas small angle light scattering was used to quantify overall domain size distribution. EPR domains from a few hundred nanometers to a few microns in size were observed with average sizes that vary from the edge to the center of the polypropylene particle. In addition, it has been observed that the morphology shifts from discrete domains to bicontinuous as the EPR content is increased. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 452–457, 2000

**Key words:** polypropylene; morphology characterization; bimodal distribution; atomic force microscopy; small angle light scattering

## INTRODUCTION

Polypropylene (PP) is one of the most important commercial polymers available because of its extremely broad spectrum of application. Pure PP however is too brittle for applications such as automotive components that require a polymer with high impact resistance. To impart toughness to relatively brittle polymer matrices, discrete rubbery domains are often added.<sup>1,2</sup> For PP, ethylene-propylene rubber (EPR) domains are added to significantly improve toughness, creating a composite known as high-impact PP.

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) have been traditionally used to study morphology development in these materials.<sup>3–6</sup> Nomura et al.<sup>3</sup>

observed rubbery domains in PP–EPR composites using TEM. To do so, ultrathin sections were prepared by microtoming the sample and staining with ruthenium tetroxide (RuO<sub>4</sub>) vapor for 4 h, providing contrast between the rubber domains and the PP matrix. Yokoyama and Ricco<sup>4</sup> have studied morphology of high-impact PP using TEM with similar sample preparation methods. In these studies, both discrete and continuous morphologies of EPR within the PP matrix were observed in samples with similar EPR contents. Although TEM provides some contrast between phases, the contrast decreases significantly in samples with high EPR content.

SEM has also been used to characterize the morphology of high-impact PP.<sup>5</sup> In these studies, samples were prepared by brittle fracture under liquid nitrogen. The SEM images show the EPR domains dispersed in PP of size 2–3 μm for samples with EPR content less than 15%. At higher concentrations, larger domains were observed. Debling<sup>6</sup> has studied the morphology of the PP–EPR systems of varying EPR ranging from 15 to

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70% EPR at various magnifications. These studies indicate the presence of pores and show that EPR domains fill the pores differently as the concentration of EPR increases. SEM studies on thin sections stained with RuO<sub>4</sub> show distinct EPR domains in the 15% EPR sample and continuous morphology in the 70% EPR sample. SEM was able to give good contrast over a wide range of EPR content; however, ruthenium was found to pool in the cavities present in the polymer, influencing interpretation of their images.

Although TEM and SEM are useful techniques for studying EPR domain morphology, they require tedious sample preparation methods. Both SEM and TEM require ultramicrotoming at cryogenic temperature to obtain very thin samples for analysis. Samples must be coated with a layer of carbon or gold for SEM, or stained using a staining agent for TEM. These difficulties drive the need for simpler experimental methods for investigating the morphology of polymer blend systems.

Atomic force microscopy (AFM) is a powerful tool for studying morphology of a variety of polymers because unlike electron microscopy techniques, AFM does not require staining or ultrathin sample slices. Though early studies using AFM were aimed at characterizing topographical features, the addition of new capabilities such as Force Modulation™ (FM; Digital Instruments, Santa Barbara, CA) has substantially broadened the range of application. A review of different AFM techniques applicable to polymer systems is presented by Maganov and Heaton.<sup>7</sup> FM creates a map of the surface composition based on differences in surface elasticity. In previous studies, force modulation has been used to study the surface composition of organic films<sup>8</sup> and phase separation in copolymer blends.<sup>9</sup> FM has been used primarily as a qualitative tool to obtain relative contrast between phases; however, in a recent study, a method for quantifying the relative measurements of surface elasticity for the PP-EPR system has been developed.<sup>10</sup>

Though AFM can readily identify EPR domains, it is difficult to obtain good statistical information about average EPR domain size or size distribution. To do so would require a large number of individual AFM measurements. Small angle light scattering (SALS) however is a bulk technique that provides statistical information in a single measurement and is sensitive to the micron-size range appropriate for our studies.<sup>11</sup> In previous studies, SALS has been used to observe

spherulite formation in polymers<sup>12,13</sup> and has been used to study inhomogeneities in polymer solutions.<sup>14,15</sup> In addition, heterogeneities in polymer blends have been studied and two-phase structures have been characterized using SALS.<sup>16</sup> Together, AFM and SALS can be a very effective combination for investigating the morphology of high-impact PP.

## EXPERIMENTAL

### Materials

High-impact PP used in this study was obtained from Mitsubishi Chemical Corporation, Japan, including commercial grades with EPR content ranging from approximately 5% to approximately 25% by weight. Epoxy resin for preparing molds was obtained from Struers, Inc. Ortho-dichlorobenzene and metaxylene used for index matching were obtained from Aldrich.

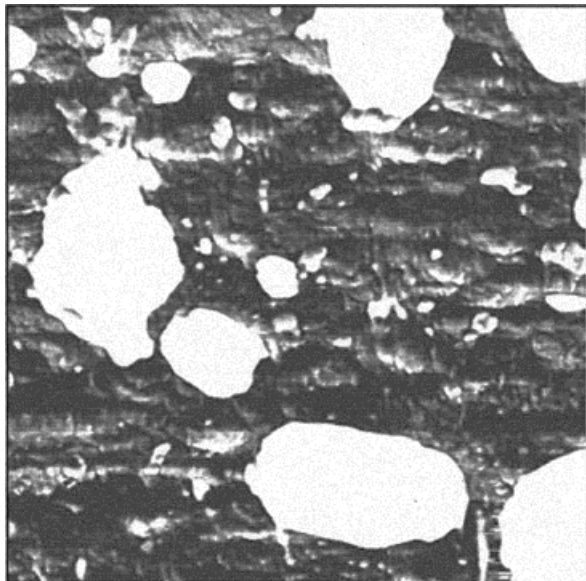
### Sample Preparation

For AFM studies, samples were first embedded in an epoxy mold to enable microtoming. The samples were mixed with the resin and cured for 24 h at room temperature before they were microtomed with glass knives. For SALS studies, the high-impact polymer was placed between glass slides, heated for approximately 30 s, and then cooled in air. The resulting thin layer of polymer was then removed from the glass slides. A small strip of polymer was then cut and placed in a sample holder with an index-matching solvent of 30% ortho-dichlorobenzene and 70% metaxylene to minimize scattering from the PP-air interface.

### Methods

#### AFM

AFM studies were performed using a Multimode AFM with a Nanoscope IIIa controller manufactured by Digital Instruments, Inc. FM in negative lift mode was employed using FESP tips with spring constants in the range of 1 to 5N/m. To obtain a good topographic image, the AFM was first engaged in tapping mode. FM in negative lift mode was subsequently engaged using a negative lift of -5 nm; however, depending on the tip used, this parameter was increased to a maximum of -15 nm to enhance the contrast. The AFM was



**Figure 1** Force modulation image of 15% EPR sample. Scan size is 5.5  $\mu\text{m}$ .

calibrated to show softer regions in light color and stiffer regions in dark color.

### SALS

For light scattering the sample stage was designed to collect data from  $2^\circ$  up to  $12^\circ$  from the incident angle. The laser source was a 0.5 mW 632.8 nm helium-neon laser and the detector was a two-dimensional charge-coupled device (CCD) with a resolution of  $512 \times 512$  pixels manufactured by Princeton Instruments, Inc. A beam stop was used at angles less than  $2^\circ$ . The data from the detector was exported to a Macintosh and analyzed using Igor Pro (Version  $\pi$ , Wavemetrics Inc.) by radially averaging the raw data to give the radial distribution of scattered intensity. The radial distance was converted into scattering vector  $q$ , defined as  $q = (4\pi/\lambda)\sin(\theta/2)$ , where  $\lambda$  is the wavelength of light and  $\theta$  is the scattered angle, using a calibration grid of known angular scattering properties. This grid was also used to verify the focus and to minimize spherical aberrations introduced by the optics. Commercially available colloidal standards 1  $\mu\text{m}$  and 3  $\mu\text{m}$  in diameter obtained from Interfacial Dynamics Inc. (Portland, OR) were used to verify the calibrations.

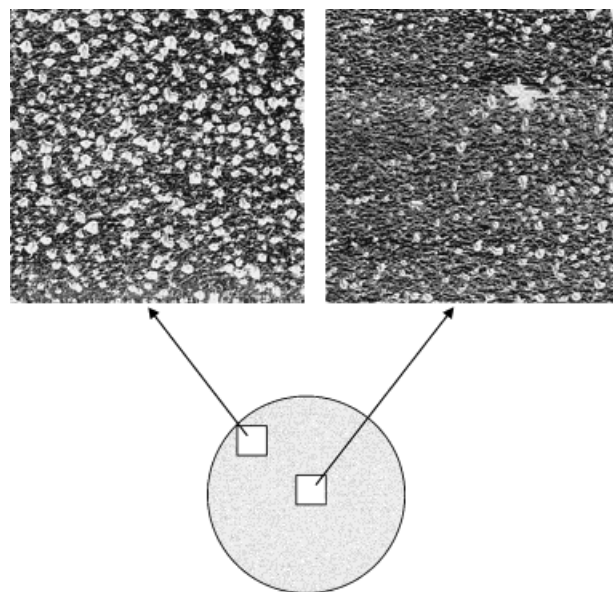
## RESULTS AND DISCUSSION

The initial goal of our AFM investigations was to test the ability of force modulation to distinguish

two, chemically quite similar, phases. Figure 1 shows that indeed EPR domains can be clearly seen within the PP matrix for a sample containing 15% EPR. Because the EPR domains are soft relative to the surrounding PP matrix, lighter white regions correspond to EPR and the dark regions correspond to the PP matrix. Figure 1 indicates that the EPR domains are distinct and range from microns down to a few hundred nanometers in size. It can also be seen that EPR domains are polydisperse and nonuniform in cross section although most can be approximated as spherical in shape.

Figure 1 was taken near the edge of the 800- $\mu\text{m}$  diameter high-impact PP particle but scans were also performed at different positions. As shown in Figure 2, scans performed near the particle edge are quite different than those at the center. Near the particle center, EPR domains are of smaller size and are separated by distances larger than those at the particle edge.

Though this illustrates that AFM in force modulation can be used to characterize EPR domains in cross section, determination of a statistically meaningful domain-size distribution via this technique would be time consuming. A technique that instead measures relatively large regions of the sample in a bulk manner such as SALS is better suited if average domain size information is required. SALS was therefore used to characterize the bulk morphology of the PP-EPR copol-



**Figure 2** Distribution of EPR domains in a 15% EPR sample. Scan size is 50  $\mu\text{m}$ .

ymer composite. The aim of these studies is to determine the ability of light scattering to characterize EPR domain distribution and develop the appropriate SALS models for data interpretation. Once appropriate models are developed, the technique can be applied to understand morphology development during the domain growth process.

Our AFM images indicate that the average EPR domain can be approximated as a sphere and that the EPR domains are not monodisperse in size. Figure 2 also indicates that the EPR domain distribution may be bimodal with an average smaller domain size near the particle center and average larger domain size near the edge. Because SALS will measure both distributions simultaneously, our model must account for both. To account for polydispersity, the Schulz model<sup>17</sup> has been commonly used where:

$$F_N(a) = (z + 1)^{z+1} x^z \frac{e^{-(z+1)x}}{\bar{a}\Gamma(z + 1)} \quad (1)$$

$F_N(a)$  is the normalized probability of occurrence of particles of radius  $a$ ,  $\bar{a}$  is the mean particle size,

$$x = a/\bar{a},$$

$$z = (1 - s^2)/s^2,$$

$$s = \sigma/\bar{a},$$

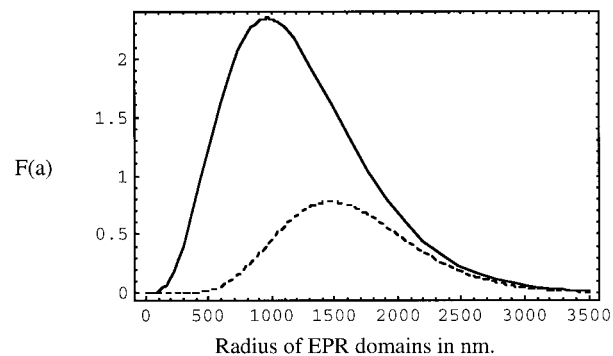
and  $\sigma^2$  is the variance.

To account for the bimodal size distribution observed by AFM, we have extended the Schulz model as:

$$F_N(a_1, a_2) = \frac{A_1 F_{N1}(a_1) + A_2 F_{N2}(a_2)}{A_1 + A_2} \quad (2)$$

where the subscripts 1 and 2 represent two different distributions and  $A_1/(A_1 + A_2)$  and  $A_2/(A_1 + A_2)$  represent the fractional contribution of each.

In a SALS experiment, the scattered intensity  $I(q)$  is typically expressed in terms of a form factor  $P(q)$  which provides information about particle size and shape and a structure factor  $S(q)$  which accounts for particle distribution. In a dilute system however,  $I(q) \approx P(q)$  and by approximating the particle shape to a known geometry, information about particle size can be obtained from fitting scattering data to form factor models.



**Figure 3** Volume-normalized size distribution of 5 and 15% EPR obtained from a Schulz model fit.

An analytical expression for the form factor for polydisperse spheres with a Schulz distribution has been derived by Corti<sup>18</sup>:

$$P(q) = \frac{9}{2z_1 q^6} \left\{ z_1 \left[ 1 - \frac{\cos(z_1 w)}{(1 + 4u^2)^{z_1/2}} - \frac{2q \sin(z_2 w)}{(1 + 4u^2)^{z_2/2}} \right] + q^2 z_2 \left[ 1 + \frac{\cos(z_3 w)}{(1 + 4u^2)^{z_3/2}} \right] \right\} \quad (3)$$

where  $u = q/z_1$ ,  $w = \arctan(2u)$ , and  $z_j = z + j$ .

From this, the form factor for a bimodal Schulz distribution can be expressed as:

$$P(q) = \frac{A_1}{A_1 + A_2} P_1(q) + \frac{A_2}{A_1 + A_2} P_2(q).$$

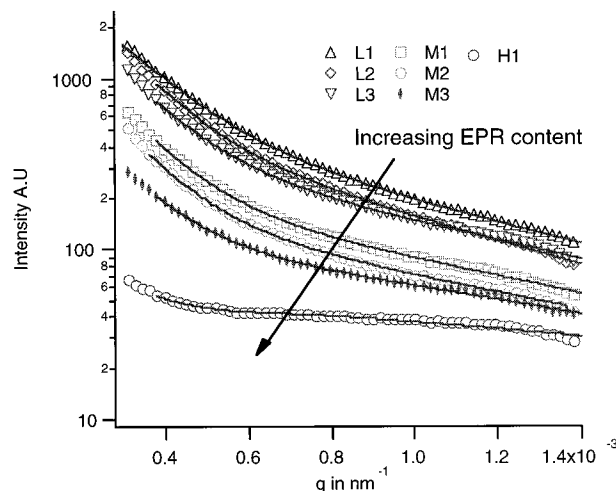
As discussed previously, at low concentrations,  $I(q) \approx P(q)$  and the light scattering data can be fit to this analytical expression for the form factor. From these fits, parameters  $z$  and  $a$  are used to obtain the number-normalized EPR domain size distribution  $F_N(a)$  [Eq. (2)]. Because smaller particles have less EPR than large particles, this number distribution is converted to a volume-normalized distribution  $F_v(a)$  of domains of a given size via:

$$F_v(a) = \frac{V(a)F_N(a)}{\int F_N(a)V(a) da}$$

where  $V(a) = (4/3)\pi a^3$ .

Figure 3 illustrates volume-normalized distributions for 5 and 15% EPR samples where the 15% EPR sample has been multiplied by 3 in order to plot the 15 and 5% samples together.

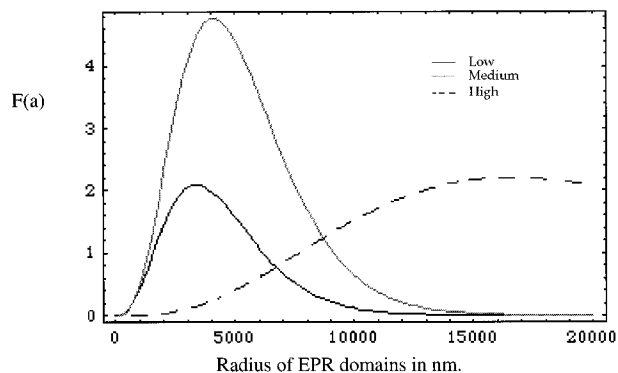




**Figure 4** Scattering data from concentration series and fit to bimodal Schulz model.

These results indicate that the majority of EPR domains lie in the size range of 1 to 3 microns; however, these distributions also show the presence of a significant number of domains of much smaller size. These results correspond well to the size range of EPR domains observed by AFM, providing a check on those studies.

To investigate the development of EPR domain morphology during polymerization, a series of samples with EPR content ranging from approximately 5% to approximately 25% by weight was studied. Our goal was to determine the feasibility of using AFM and SALS to observe any transition in morphology as the amount of EPR increases. For our SALS investigations, data was collected from four different measurements, averaged, and then repeated to confirm the consistency of the observed data. The scattering data was subsequently analyzed and fit to the bimodal Schulz model as shown in Figure 4. In this figure, it can be seen that the scattering curves for the low concentration samples are similar in shape, indicating that morphology in these samples is similar. The scattering curves also indicate a shift toward lower  $q$  as EPR content increases, suggesting a growth in the average domain size. The data for the high EPR content sample is significantly different than the other samples however, indicating that this sample has a very different structure than the other samples. This is confirmed in Figure 5 where the volume-normalized distributions for the sample with high EPR content is shifted toward very large particle sizes. This suggests the morphology in this sample may

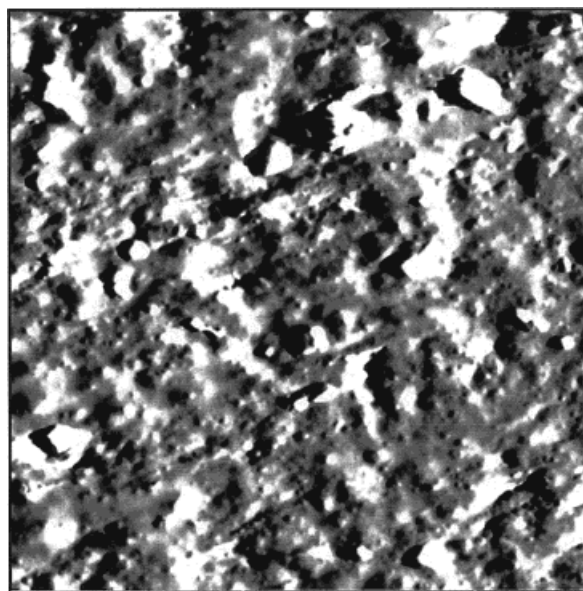


**Figure 5** Volume-normalized distribution for the concentration series from the bimodal Schulz model.

be bicontinuous, a hypothesis that is encouraged by examining the AFM image for the high EPR content sample shown in Figure 6. In this image, both large continuous and discrete EPR domains can be seen.

To confirm this observation, a different method of analysis was used for the high EPR content sample. The Debye–Bueche model,<sup>19</sup> a model commonly used to fit scattering data from bicontinuous systems,<sup>20</sup> was used to analyze the scattering data. This model can be expressed as:

$$I(q) = \frac{I(0)}{(1 + q^2 a_c^2)^2}$$



**Figure 6** AFM image of high EPR content sample indicating a bicontinuous morphology. Scan size is 25  $\mu\text{m}$ .

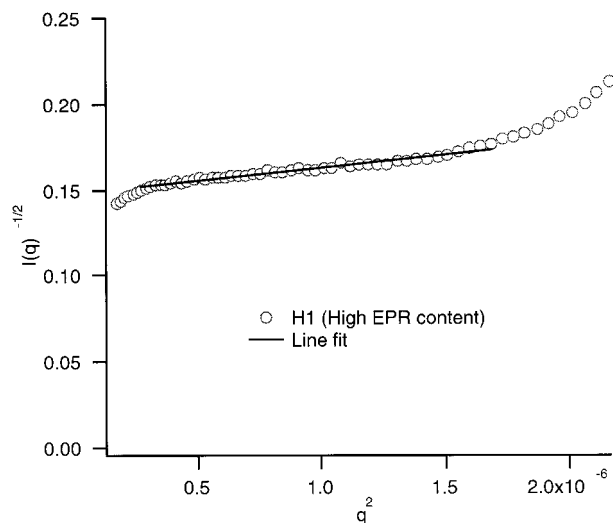


Figure 7 Debye-Bueche plot.

where  $a_c$  is a correlation length and  $I(0)$  is the intensity at zero  $q$ . A plot of  $I(q)^{-1/2}$  versus  $q^2$ , known as the Debye-Bueche plot, will be a straight line if the system morphology is bicontinuous. Such a plot for the high EPR content sample is shown in Figure 7.

The linear fit at low  $q$  indicates that morphology in the high EPR content case resembles a bicontinuous morphology at larger domain sizes. The data at high  $q$  probably indicate the presence of discrete domains at smaller length scales. These observations and the earlier AFM studies lead to the conclusion that the morphology is gradually shifting toward that of a bicontinuous morphology at high EPR concentrations.

## CONCLUSIONS

It has been shown that AFM is a useful tool in identifying EPR domains in a PP matrix. Distinct domains of EPR were observed at low and medium EPR content with sizes ranging from a few hundred nanometers to a few microns. The EPR distribution was found to be polydisperse and vary with position within the high-impact PP particle. At higher concentration, the morphology was found to shift toward a bicontinuous structure; however, small discrete domains remained. To obtain statistically relevant information about domain size distribution, SALS was used. A vari-

ation of the Schulz model was used to analyze the scattering data for a bimodal, polydisperse distribution, providing information on both EPR domain size as well as size distribution.

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