ATOMIC FORCE MICROSCOPY AND SMALL ANGLE LIGHT SCATTERING STUDIES OF HIGH IMPACT POLYPROPYLENE

By

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ABSTRACT

High impact resistant polypropylene is one of the most important commercial polymers because of its wide variety of applications. The properties of this material depend on the morphology of ethylene-propylene rubber (EPR) domains used as an impact modifier within the polypropylene matrix. Current characterization methods employed to investigate the morphology of these materials involve tedious experimental methodologies and have not been very successful in characterizing the morphology of the copolymer efficiently.

This work examines the utility of two techniques in characterizing the morphology of the copolymer composite. Atomic force microscopy (AFM) and small angle light scattering (SALS) were employed, both of which are relatively simple compared to previously used methods. The ability of the AFM to characterize copolymer composites was established and EPR domain distribution within the polypropylene matrix was studied. Mass transfer limitations, that could significantly affect EPR domain morphology, were also investigated. It was found that no significant resistances to mass transfer are apparent. A methodology to study morphology of copolymer using SALS
was also established. SALS studies provided information on size distribution of EPR domains and indicate a change in morphology towards a bicontinuous morphology as the EPR content was increased, supporting our AFM observations.
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\( a \) \quad \text{Particle radius}

\( a_c \) \quad \text{Debye-Bueche correlation length}

\( A_1,A_2 \) \quad \text{Schulz model scaling parameters}

\( I \) \quad \text{Scattered intensity}

\( P \) \quad \text{Form factor}

\( t \) \quad \text{Time}

\( v \) \quad \text{Velocity}

\( V \) \quad \text{Volume}

\( x \) \quad \text{Distance}

\( z \) \quad \text{Schulz model width parameter}

\( q \) \quad \text{Scattering vector}

\( \lambda \) \quad \text{Wavelength of light}

\( \theta \) \quad \text{Scattered angle}
Chapter 1

INTRODUCTION

Background

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

Commercial production of impact resistant polypropylene is a multistage process. Typically, propylene is polymerized to polypropylene in the first stage and then passed to a second reactor. This homopolymer is then further reacted with a mixture of ethylene and propylene which diffuse inside the polypropylene matrix to form domains of EPR.
In Mitsubishi Chemical Corporation’s (MCC) continuous process, propylene is first polymerized to polypropylene using Ziegler-Natta catalyst\textsuperscript{3} in a gas phase reactor, though liquid phase and slurry phase reactors are used in other commercial processes. The homopolymer is then passed through a classifier to separate the desired size range of particles and the classified particles are fed to the EPR reactor which is a gas phase fluidized bed reactor. Ethylene and propylene are introduced in this reactor and they diffuse into the homopolymer matrix and form domains of EPR. A schematic representation of the process is given in Figure 1.1.

**Motivation**

As discussed above, EPR domains are added to improve the impact resistance of the polypropylene matrix. These domains possess a different rigidity than the surrounding polypropylene matrix and act as stress-concentrators\textsuperscript{2,4}. On impact, the EPR domains absorb energy and yield preferably thereby preventing the polypropylene matrix from rupturing. In this process, the size and distribution of the EPR domains is vital because it controls the properties of the final product. For example, a larger number of small EPR domains can effectively absorb more impact energy than a few large EPR domains. It is therefore necessary to optimize the size and distribution of EPR domains within the PP matrix to achieve desired impact resistance characteristics.
Figure 1.1 Schematic representation of the high-impact polypropylene process
High impact polymer produced by the continuous process has a broad distribution of copolymer composition among various particles due to a broad residence time distribution in the reactor. This can cause some particles to be predominantly EPR leading to the formation of “gel” which has an adverse effect on the quality of the product. High gel content reduces both the impact strength of the polymer and the bulk density of the final product.

To understand the effect of process parameters on EPR domain morphology, modeling has been widely employed. To better control EPR domain growth, models have been developed which incorporate mass and heat transfer effects, kinetics of polymerization, and particle morphology. In these, it is particularly important to understand the role of mass transfer in order to predict particle growth and morphology development. Mass transfer limitations influence the size and distribution of EPR domains in the homopolymer as well as the molecular weight distribution of the copolymer in the polypropylene matrix, both of which have a significant effect on the processability of the final impact copolymer. Further development of current models will require significant improvement in our understanding of morphology in these systems.

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) have been primarily used to study morphology development in these materials. These techniques however require tedious sample preparation methods like ultra-
microtoming and staining. Atomic force microscopy (AFM) however is a powerful tool that can differentiate EPR domains from polypropylene, even at very small length scales and does not require ultra thin slices or staining. Small angle light scattering (SALS) is another simple technique that can be used in combination with AFM studies to obtain quantitative information about EPR domain morphology.

**Research Objectives**

The aim of this research is to investigate the use of recently developed AFM techniques in combination with light scattering to characterize the morphology of EPR domains in a polypropylene matrix. AFM studies will focus on directly studying the distribution of EPR inside the polypropylene matrix and will help determine if any mass transfer limitations exist in the polymerization reaction. Light scattering studies will compliment the surface-oriented AFM studies to obtain quantitative information about EPR domain size and distribution. SALS studies will focus on deriving size distributions of EPR using both established and new light scattering models. Together, these studies will aid our understanding of morphology development in PP-EPR composites.
Chapter 2

BACKGROUND

High impact polymers have been widely studied over the years because of their commercial importance. Much of the research however has been conducted in industry and the publications are restricted. This chapter outlines previous work on characterizing morphology of high impact polymers and the experimental methods typically used to characterize morphology within these materials.

Electron microscopy techniques

Morphology of high impact polypropylene has been conventionally characterized using electron microscopy techniques. Both scanning electron microscopy (SEM) and transmission electron microscopy (TEM) have been used to characterize morphology of high-impact polypropylene.

Rostami and Riew discuss several high impact polymer systems that have been characterized using SEM or TEM. Work has been published on other impact
polymers\textsuperscript{6,7}, however, limited work has been published on characterization of high impact polypropylene. Nomura et al.\textsuperscript{8} have observed rubbery domains in PP-EPR composites using TEM. To do so, ultra-thin sections were prepared by microtoming the sample and staining with ruthenium tetroxide (RuO\textsubscript{4}) vapor for 4 hours. This gave contrast between the rubber domains and the polypropylene matrix. Yokoyama\textsuperscript{9} has studied morphology of high impact polypropylene using TEM with similar sample preparation methods. In these studies, both discrete and continuous morphologies of EPR within the polypropylene matrix were observed in samples with similar EPR contents. Although TEM gives contrast between the two phases, the contrast was not significant in samples with high EPR content.

SEM has also been used to characterize the morphology of high-impact polypropylene\textsuperscript{10}. In these studies, samples were prepared by brittle fracturing under liquid nitrogen. The SEM images show the EPR domains of size 2 -3 μm dispersed in the polypropylene for samples with EPR content less than 15%. At higher concentrations larger domains were observed. Debling\textsuperscript{5} has studied the morphology of the PP-EPR systems of varying EPR content ranging from 15% EPR to 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\textsubscript{4} 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 studies.

Although TEM and SEM are useful techniques to study EPR domain morphology, they require tedious sample preparation methods. Both SEM and TEM require ultramicrotoming at cryogenic temperature to obtain ultrathin samples for analysis. Samples must be coated with a layer of carbon or gold for SEM, or stained using a staining agent for 4 hours for TEM. The RuO₄ used for staining has also been found to pool in the cavities present in the sample in some cases. These difficulties drive the need for better experimental methods for studying the morphology of polymer blend systems.

**Other characterization methods**

Although TEM and SEM are currently the primary techniques used for characterizing the morphology of high-impact polypropylene, other methods have also been used to compliment electron microscopy techniques, including optical microscopy, thermal methods and chemical methods.

Optical microscopy is not very effective in studying high impact polymer composites; however, the technique has been used in some cases to complement other
techniques\textsuperscript{9,11,12}. DSC has also been used to measure glass transition temperatures which have been found to decrease with increasing EPR content\textsuperscript{8}.

Chemical imaging is one of the latest methods used to characterize impact copolymer. For example, the surface architecture of high impact polypropylene coated with chlorinated polypropylene has been studied recently using fluorescence and Raman chemical imaging\textsuperscript{13}. Fluorescence imaging uses a fluorescent dye to differentiate EPR domains from chlorinated polypropylene on the basis of large variations in the fluorescence quantum efficiency between EPR and chlorinated PP. The samples are doped with fluorescent Nile red and imaged with a confocal microscope. These studies show EPR domains on the order of a few microns, and indicate the migration of EPR towards the chlorinated polypropylene surface. Fluorescence imaging has been performed only on the chlorinated polypropylene surface however and its ability to distinguish EPR from regular polypropylene is not known.

Raman imaging has been used to complement fluorescence imaging to obtain qualitative information\textsuperscript{13}. In Raman imaging, the Raman spectrum is analyzed at increasing depths from the surface providing information on relative EPR content. Raman imaging however is limited by the spot size of illumination and hence does not give useful information about particles smaller than a few microns.
Modeling as a tool to understand morphology

Since limited information on the factors affecting morphology is known, modeling has been extensively employed as a tool to understand morphology development in these materials. The use of models allows one to test the effect of different physical and chemical factors influencing morphology of the composite copolymer. Models incorporate process phenomena such as heat transfer, fluid flow and reaction kinetics along with process parameters including pressure and temperature to predict the morphology of the final product.

Modeling the PP-EPR system involves numerous assumptions and approximations; however, with the help of powerful computers, modeling has become a powerful tool to understand morphology. Initial models have focused on the growth of polypropylene particles and included the effect of mass transfer resistances and heat transfer resistances. Subsequently, these models have been extended to include the growth of the copolymer in the polypropylene matrix.

The simplest model describing the polymerization of polypropylene is the polymeric core model which was developed based on the solid core model\textsuperscript{14}. This model assumes that the catalyst sites expand as the polymer is formed and predicts a distribution of the molecular weights within the polymer. Using this model, the effects of catalyst
fragmentation on domain size and structure have been studied\textsuperscript{15,16}. Though this model is primarily aimed at the initial formation of polypropylene and is not applicable to the copolymerization reaction, this model does form the basis for more sophisticated approaches subsequently developed.

The model that has been most effectively applied to the PP-EPR system is the multigrain model\textsuperscript{17-19}, which accounts for two levels of mass and heat transfer resistances. This model assumes the presence of micro-particles in the polymer particles which consist of the catalyst sites and predicts increasing mass transfer limitations as the microdomains grow in size. The model has been simplified by assuming the particle consists of layers instead of small spherical domains\textsuperscript{20-23} and in doing so has been able to explain domain growth more effectively than earlier models.

Although modeling is a powerful tool that can simulate a variety of conditions and predict how particle morphology changes, it is incomplete without proper physical evidence and input. Modeling is therefore a good tool to complement experimental methods which provide useful information to use in the models. For example, current models on mass transfer predict different distributions of EPR domains based on different assumptions. If the distribution of EPR can be studied directly, it can be used to help identify the appropriate model or to modify models to obtain significantly better results.
**Atomic force microscopy**

Atomic force microscopy is a powerful technique used to characterize polymeric systems but is also applicable to a wide variety of materials ranging from metals to biological samples. The AFM can give useful information about the surface including topography and surface composition and does not require tedious sample preparation methods or staining as do the electron microscopy methods.

AFM images surface topography by tracking the deflection of a small tip as it travels across the sample. The tip deflects up when it encounters a tall feature in the sample and it extends down if a low feature is encountered. This mode of operation has been extended to characterize surface composition based on differences in the surface elasticity. In this method, known as force modulation mode, the tip is made to indent the sample. Indentation is different for hard sample and soft samples; hence, a different feedback is obtained from two components with different surface elasticity. Using this, a map of the relative surface elasticity can be obtained. Chapter 3 discusses the principle and modes of operation of the AFM in detail.

A review of the different AFM techniques applicable to polymer systems is presented by Maganov\(^2^4\). In previous studies, force modulation has been used to study the surface composition of organic films\(^2^5\) and phase separation in copolymer blends\(^2^6\).
Another mode, phase imaging, has been successfully used to study the morphology of high impact polypropylene modified with an ethylene-butene rubber. Force modulation has been primarily used as a qualitative tool to obtain relative contrast between phases; however, in a very recent study, a method for quantifying the relative measurements of surface elasticity for the PP-EPR system has been developed.

**Small angle light scattering**

Light scattering is a popular technique for characterizing polymer morphology. When light interacts with a particle, it is scattered from its original direction of propagation. The scattering is a function of the wavelength of the light, the size and shape of the particles that scatter, the optical properties of the medium and the angle of scattering. If the optical properties of the medium are known, scattered intensity from light of known wavelength can be used to obtain information about the size and shape of the particles. Typically, particle shape is approximated with a known geometry which allows information about particle size to be calculated.

Small angle light scattering (SALS) is often used for characterizing colloidal dispersions since they lie in the micron size range observable by this technique. SALS has also been used to observe spherulite formation in polymers and has been used to study inhomogeneities in polymer solutions. In addition, heterogeneities in polymer
blends have been studied and two-phase structures have been characterized using SALS\textsuperscript{34}.

SALS is an ideal tool for investigation of the bulk morphology of the PP-EPR system since EPR domains lie in the appropriate size range. SALS can be used to obtain information about the length scales and distribution of EPR domains within the PP matrix. In addition, by looking at a number of samples, one can use SALS to obtain information on how morphology develops with EPR content in the system.

While SALS provides information about bulk morphology, atomic force microscopy provides information about surface physical properties. Using this technique, EPR domains distributed within a polypropylene matrix can be studied. Such studies will help in understanding mass transfer limitations and provide useful input to modeling. Together, AFM and SALS can be a very effective combination for investigating the morphology of high-impact polypropylene.
Chapter 3

EXPERIMENTAL METHODS

This chapter describes the experimental methods used in our studies to investigate morphology of impact copolymer. In this, the two primary techniques used, atomic force microscopy and small angle light scattering, are discussed.

**Samples:**

Samples used for our studies were obtained from Mitsubishi Chemical Corporation, Japan. Relevant details of samples used for our studies have been given under each section.

**Atomic force microscopy**

Atomic force microscopy (AFM) was used to characterize the morphology of the composite because for samples of little density difference, it can be much easier to use than conventional electron microscopy techniques such as transmission electron microscopy (TEM) or scanning electron microscopy (SEM). AFM does not require ultra-
thin slices or preferential staining and yet can identify EPR domains at very small length scales based on differences in surface modulus. AFM provides a map of topographical features which both SEM and TEM are not capable of imaging. AFM is also capable of imaging samples under ambient conditions at atmospheric pressures and in liquid.

**Principle**

AFM images surfaces and surface properties with a small cantilever that deflects due to the force of interaction between the tip and the sample surface. The deflection of the tip is tracked by a laser and a photo detector and converted to different types of images depending on the feedback from the tip. This is shown schematically in Figure 3.1.

![Figure 3.1 Principle of AFM](image)

**Figure 3.1** Principle of AFM\(^{35}\).
Components of AFM

The atomic force microscope consists of a scanning system, a probe, a probe motion sensor and an electronic interface. The scanning system consists of a piezoelectric tube scanner that expands or contracts proportional to an applied voltage. The scanner consists of three independently operating piezo-electrodes which can scan independently in the x, y and z directions. The probe consists of a tip integrated with a cantilever and is assembled of silicon or silicon nitride typically produced by etching. Cantilever selection depends on the sample and the important parameters that characterize the probe are the spring constant and resonant frequency. A SEM image of a typical silicon cantilever and tip assembly is shown in Figure 3.2 (a) and the shape of a typical tip is shown in Figure 3.2 (b).

Figure 3.2 (a) SEM image of a silicon AFM tip.\textsuperscript{35}

Figure 3.2 (b) A typical silicon tip used for force modulation.\textsuperscript{35}
A probe motion sensor system senses the tracking parameter which can be deflection or change in oscillation amplitude depending on the mode of operation and provides feedback to the piezoelectric scanner to keep the parameter at a set value. The most commonly used system is the beam deflection system that uses a laser reflecting off the tip and onto a split-diode photo detector. The electronic interface accepts the signal from the probe motion sensor and contains the feedback control system that provides the control signal voltage to the piezoelectric scanner.

Operating Modes

The AFM can be operated in different modes depending on the type of information one is interested in obtaining. These modes utilize the same principle of the tip scanning the surface, but differ in the way the scan is made.

Contact mode:

One of the first methods of AFM imaging was contact mode. In this mode the tip is in contact with the sample throughout the scan. As the scan is made, the tip deflects and the piezo scanner moves in the z direction to keep the deflection of the tip at its set point value. A topographical image of the surface is created from the extent of deflection at each point. Figure 3.3 illustrates contact mode.

Though this technique allows very high resolution, the major drawback is that contact of the tip with the sample can damage both the tip and the sample surface. Also,
under ambient air conditions, most surfaces are covered by a layer of adsorbed gases (condensed water vapor and other contaminants). When the tip comes into contact with this layer, capillary action causes a meniscus to form and the surface tension pulls the cantilever down into the layer. This creates an additional adhesive force between the tip and the sample and can distort the measurement of data.

**Tapping Mode:**

Tapping mode (TM) imaging overcomes many of the limitations of contact mode operation. In tapping mode, the tip is oscillated at a desired frequency (usually near the resonant frequency of the cantilever). The resonant frequencies of typical tapping mode tips are on the order of 300 to 400 kHz and the ‘free air’ amplitude of a tapping mode cantilever is around 20 nm. When the tip is engaged and the scan is made, the tip is not in contact with the surface continuously and hence there is no damage to the surface or tip due to dragging. Tapping mode also prevents the tip from sticking to the surface, as the oscillation amplitude is sufficient to overcome the sample-tip adhesion forces. Figure 3.4 illustrates tapping. As the oscillating cantilever begins to intermittently contact the surface, the cantilever oscillation is reduced due to the contact with the surface. This reduction in oscillation amplitude is used to identify and measure surface features.
Figure 3.3 Illustration of contact mode\textsuperscript{35}.

Figure 3.4 Illustration of tapping mode\textsuperscript{35}.
Force Modulation Mode:

Contact mode and tapping mode can give information about topography only. Topographical features however do not necessarily give information about compositional distribution within a sample. Force modulation (FM) imaging is a technique that identifies and maps differences in surface stiffness or elasticity. The technique utilizes contact mode or tapping mode with a special type of cantilever holder that has a piezoelectric bimorph which can oscillate at low frequencies of the order of 10-25 kHz. In this mode, imaging is done with a small vertical (z) oscillation that is significantly faster than the scan rate. Figure 3.5 illustrates force modulation mode.

In the contact mode version of force modulation imaging, the force on the sample is modulated about the set point scanning force such that the average force on the sample is equivalent to that in simple contact mode. When the probe is brought into contact with a sample, the surface resists the oscillation and the cantilever bends. Under the same applied force, a stiff area on the sample will deform less than a soft area; i.e., stiffer surfaces cause greater resistance to the vertical oscillation and, consequently, greater bending of the cantilever. The variation in cantilever deflection amplitude is a measure of the relative stiffness of the surface.

The contact mode version of force modulation inherits the disadvantages of contact mode. The latest form of force modulation imaging utilizes tapping mode and a technique known as interleave mode. This method, known as “negative lift mode”, gives better
resolution than the contact mode force modulation. In this method, one engages using
tapping mode and a good topographical image is obtained. When negative lift is engaged,
the first topographical scan line is followed by the interleave scan which is performed at a
fixed depth below the original topographic scan. This causes the tip to indent the surface
and the feedback amplitude gives a measure of the relative surface stiffness. Typically,
negative lift values between –5 and –10 nm are used.
Figure 3.5 Principle of force modulation mode\textsuperscript{35}.
The selection of a suitable cantilever depends on the stiffness of the sample being probed. Typically, softer samples such as biological tissues require cantilevers with low spring constants (0.02 – 0.1 N/m) while polymeric samples typically require cantilevers with higher spring constants (1-5 N/m). To study the PP-EPR copolymer, force modulation tips manufactured by Digital Instruments were used. These cantilevers were 225 μm in length and had a spring constant between 1 and 5 N/m.

**Limitations**

The AFM is a very powerful tool that has broad applications ranging from characterizing surface morphology to measuring forces of interaction between particles. It has been applied to a wide variety of materials ranging from polymers to metallic surfaces. However, AFM requires a relatively flat surface with roughness on the order of microns. This often necessitates microtoming one surface of the sample to achieve a sufficiently smooth surface.

**Sample Preparation**

The high impact copolymer samples studied were typically around 500 μm in size with the EPR domains distributed inside them. Since AFM requires a flat surface, samples were first embedded in an epoxy mold to enable microtoming. Two different
epoxy resins were used. Eponate-12 epoxy resin by Ted Pella, Inc. was first tried, but this required curing at high temperature that could affect the system morphology. A different epoxy resin, Epofix epoxy kit, manufactured by Struers Inc., was therefore used. This epoxy resin cured at room temperature and hence should not have altered the morphology of the polymer composite.

The samples were cured for 24 hours at room temperature before they were microtomed. A standard manual microtome with glass knives was used and was able to slice through both the epoxy mold and the embedded particles. Figure 3.6 shows an optical image of the impact polymer particles embedded in the epoxy after microtoming. With efficient microtoming, a smooth surface with roughness on the order of a few hundred nanometers could be created.
Figure 3.6 Optical image of microtomed PP sample embedded in epoxy.
Small Angle Light Scattering

Small-angle light scattering (SALS) was used to study the bulk morphology of the copolymer composite. Typically, light scattering studies provide information on domain structure and domain size distributions. Light scattering studies can be simple to set up and relatively inexpensive.

Principle

When a beam of light strikes a particle, it is deflected away from the original direction depending on the interaction of the light with the particle. This phenomenon is known as scattering of light. The intensity of scattered light depends primarily on the wavelength of the incident light, the size of the scattering particles, the shape of the scattering particles, optical properties of the scattering medium and the angle of observation. Information on size and shape of scattering particles can be obtained if the variation of scattered intensity with angle is known. By approximating the size of scattering particles to a known geometry, information on size can be obtained.

Theory

In static light scattering, one measures the time-averaged scattered intensity as a function of scattered angle. The angular dependence of the scattered intensity can be used
to deduce information on internal structure including particle shape and characteristic length scale.

**Rayleigh scattering**

The first and simplest theory that explained the scattering phenomenon is the Rayleigh scattering theory. This theory was derived by Lord Rayleigh in 1871 from the fundamental principles of the interaction of electromagnetic radiation with matter. Rayleigh's theory assumes that scattering particles are small in dimension compared to the wavelength of light and explains some popular scattering phenomenon like the blue color of the sky. It is applicable to dilute solutions and is often used in determining the molecular weights of polymers.

**Debye theory**

For systems in which the particle sizes are larger and comparable to the wavelength of the light, Rayleigh theory fails. The Debye theory overcomes this by considering different regions of the same particle as scattering centers. Light scattered by these different scattering centers can interfere and a correction factor to Rayleigh scattering is introduced. The correction factor is called the *form factor* $P(\theta)$ and is a function of the angle of observation.
The Debye theory introduces another important parameter known as the \textit{scattering vector} \((q)\). If the incident light is scattered at an angle \(\theta\), then the scattering vector is defined as

\[
q = \frac{4\pi}{\lambda} \sin \left( \frac{\theta}{2} \right)
\]

where \(\lambda\) is the wavelength of the incident light.

The derivation of the scattering vector comes from fundamental radiation scattering theory. Consider a scalar electromagnetic field with incident wave vector \(\Vec{k}_i\) and the scattered wave vector \(\Vec{k}_s\).

\[\text{Figure 3.7 The scattering vector } \Vec{q}\]
The magnitude of $\vec{k}$ is obtained from fundamental wave theory. If we represent light as a wave, as shown schematically in Figure 3.8, it can be represented as

$$\Psi(x,t) = A \sin(k(x - vt))$$  \hspace{1cm} (3.2)

where

$\Psi(x,t)$ gives the profile of the wave at position $x$ and time $t$

$k$ is the scalar value of the wave vector $\vec{k}$

$v$ is the speed of wave propagation,

and $\lambda$ is the wavelength of light

Figure 3.8 Profile of wave function of light.
Since the wave function is periodic in nature, an increase or decrease in \(x\) by a wavelength \(\lambda\) does not alter the wave function. Therefore, we have,
\[
\psi(x, t) = \psi(x \pm \lambda, t)
\]
which gives \(\psi(x \pm \lambda, t) = A\sin(k[(x \pm \lambda) - vt])\).

This can be rearranged as
\[
\psi(x \pm \lambda, t) = A\sin(k(x - vt) \pm k\lambda)
\]
and since the wave function is periodic, it can be represented as
\[
\Psi(x, t) = A\sin(k(x - vt) \pm 2\pi)
\]
From 3.3 and 3.4, one obtains, \(k\lambda = 2\pi\)

Therefore, \(k = |\vec{k}| = \frac{2\pi}{\lambda}\) \hspace{1cm} (3.5)

If one assumes elastic scattering, the magnitude of the incident and scattered wave vectors will remain the same and,
\[
|\vec{k}_i| = |\vec{k}_s| = \frac{2\pi}{\lambda},
\]
then, by vector addition,
\[
|\vec{q}| = |\vec{k}_i| - |\vec{k}_s|.
\]

By the cosine rule
\[
q^2 = k_i^2 + k_s^2 - 2k_i k_s \cos(\theta)
\]
or \(q^2 = 2k_i^2(1 - \cos(\theta)) = 2k_i^2(2\sin^2(\theta / 2))\) from which \(q = 2k_i \sin(\theta / 2)\)

Since \(|\vec{k}_i| = |\vec{k}_s| = \frac{2\pi}{\lambda}\),
one obtains $|q| = \frac{4\pi}{\lambda} \sin(\theta / 2)$.

The scattering vector $q$ is important since its inverse, $q^{-1}$, represents the characteristic length scale measured in a scattering experiment under given conditions. Scattered light intensity $I(q)$ is typically written in terms of the form factor $P(q)$ and another term known as the structure factor $S(q)$ which arises due to interparticle correlations as

$I(q) = P(q)S(q)$.

The simplest light scattering model that can be applied to our PP-EPR system assumes particles to be monodisperse spheres. For a dilute solution of such spheres with radius $a$, $S(q)$ can be approximated as 1, and

$$P(qa) = \left( \frac{3\sin(qa) - qa\cos(qa))}{(qa)^3} \right)^2$$

(3.6)

The functional form of this model for monodisperse spheres is shown in Figure 3.9.
Figure 3.9 Functional form of form factor curve for monodisperse spheres.
Experimental set up

The light scattering set up consists of a laser source, a sample stage, focusing optics and a detector. The schematic of the set up is illustrated in Figure 3.10. The sample stage was designed to collect data from 2 degrees up to 12 degrees from the incident angle. The laser source is a 632.8 nm helium-neon laser and the detector is a two-dimensional CCD with a resolution of 512x512 pixels. A beam stop is included in the assembly to protect the detector from direct laser illumination at very small angles where there is scattering by large particles.

Figure 3.10  Schematic representation of light scattering set up.
Figure 3.11 shows a typical image of scattered intensity from a sample measured with the 2D CCD detector.

![Figure 3.11 Typical light scattering data showing intensity distribution. The dark region in the middle is due to the beam stop.](image)

The data from the detector is exported to a Macintosh and analyzed using Igor Pro by radially averaging the raw data to give the radial distribution of scattered intensity. The radial distance is converted to an angular measure using a calibration grid and then converted into scattering vector \( q \). The \( I(q) \) vs. \( q \) data is subsequently fit using various light scattering models.
Standards and Calibration

To convert the radial intensity distribution to a distribution in terms of the scattering vector $q$, it was necessary to use a sample with known angular scattering properties. Calibration was done using a diffraction pattern generator. A square grid generator with angular intervals of 3.5° between parallel gridlines was used. This square pattern was also used to achieve the right focus and to minimize spherical aberrations introduced by the optics. Figure 3.12 shows an image of the grid pattern recorded by the detector.

Figure 3.12 Image of a square diffraction pattern used for calibration.
To verify the calibrations, commercially available colloidal standards obtained from Interfacial Dynamics $^{38}$ were used. These colloids were available spherical in shape and monodisperse in size, and were purchased in two average sizes, 1 μm and 3 μm in diameter. These standards were also used to verify the effectiveness of models used to fit the light scattering data. Figure 3.13 shows a scattering curve from the 3μm polystyrene standard. Using the form factor model for monodispere spherical particles described previously gives a value of 3.1 μm for the mean colloid diameter.

![Figure 3.13 Scattering data and model fit for 3μm polystyrene.](image)

**Figure 3.13** Scattering data and model fit for 3μm polystyrene.
Sample Preparation

In the PP-EPR system, EPR domains are distributed throughout the polypropylene matrix. To study EPR domain morphology using light scattering, scattering from the PP-air interface must be minimized. To do this, an index-matching solvent, a mixture containing 30% by weight of ortho-dichloro benzene and 70% by weight of meta xylene, was used. The proper composition of the mixture for index matching was determined by performing a scattering study on a sample of pure polypropylene. The desired index-matching fluid composition was achieved when the transmitted intensity through the PP-fluid mixture reached a maximum.

Initial studies were performed in a glass sample holder of 5 mm path length. This path length however was too long and introduced multiple scattering. Hence, a different method of sample preparation was used for further studies. In the ‘melt-squash’ method, a small amount of polymer was placed between two glass slides in a single layer and placed over a hot plate for a short time, usually less than 30 seconds. During heating, the polymer melts between the glass and the slides are then cooled immediately in air, forming a thin layer of polymer. It is assumed that the EPR domains are not altered in shape or number because of this sample preparation method. We believe this to be a reasonable assumption since EPR domains are amorphous, do not undergo any phase transitions, and the exposure time to elevated temperature is small compared to the
diffusion time scales of polymer domains. The resulting thin layer of polymer was then removed from the glass slides after cooling. A small strip of polymer was cut and placed in a sample holder with index matching solvent, minimizing multiple scattering.

**Applicability and Limitations:**

For the PP-EPR system, the size range of the EPR domains is on the order of microns. SALS is a good tool for studying particles in this size range; however, scattering by small sub-micron size particles is not observed in the small angle studies and are not accounted for in our analysis. Scattering by particles larger than 15 μm is also not observed since the beam stop blocks scattered light at low $q$. 
Chapter 4

MORPHOLOGY CHARACTERIZATION USING

ATOMIC FORCE MICROSCOPE

Atomic force microscopy (AFM) was used to characterize the morphology of PP-EPR copolymer composites. At first, a feasibility study was conducted on two samples. The purpose of these initial studies was to establish the methodology required to investigate polymer composite morphology via AFM. This includes sample preparation methods and determining which AFM modes were useful in distinguishing EPR domains from the polypropylene matrix.

Initial Studies

Although the capability of AFM in identifying different regions in a polymer blend based on surface elasticity has been shown\textsuperscript{25,26}, it was necessary to determine its applicability towards characterizing the PP-EPR system. Initial studies were carried out using polymer samples of different EPR content to determine if AFM can identify EPR domains in a polypropylene matrix.
**Identifying EPR domains in a polypropylene matrix**

The first sample studied contained 5% EPR and was studied using force modulation (FM) mode. The AFM was first engaged in tapping mode to obtain a good topographic image, and FM in the negative lift mode was subsequently engaged using a negative lift of -5 nm. Depending on the tip used however, this parameter was increased to a higher negative lift to a maximum of -15 nm in order to enhance the contrast.

The AFM was calibrated to show softer regions in light color and relatively harder regions in dark color. Since the EPR domains are soft relative to the surrounding polypropylene matrix, lighter white regions correspond to EPR and the dark regions correspond to the polypropylene matrix (see Figure 4.1). At this length scale, this image shows EPR domains of different size distributed throughout the polypropylene matrix.
Although the images show good contrast between regions, to confirm that the white regions correspond to EPR, a sample of pure polypropylene was used as a standard. The sample was prepared under identical conditions as the 5% EPR sample and a FM image was obtained under similar scan parameters. The FM image of this sample, shown in Figure 4.2, did not show significant contrast like the previous image, even at higher resolution. This indicates the white regions in the 5% EPR samples indeed represent a different material (EPR) present in the polypropylene matrix with a different surface elasticity than the surrounding material.
These initial studies also show that EPR domains are on the order of microns or smaller and are dispersed throughout the PP matrix. The ability of the AFM to distinguish the softer EPR domains from the relatively hard polypropylene matrix has been confirmed.
**EPR distribution studies**

These initial studies show that the AFM is capable of identifying EPR domain distribution in a polypropylene matrix. Such studies can provide information on both the length scales of the domains and qualitative information about their morphology. To perform these studies, a sample containing 15% EPR was studied at different scan sizes and in different regions within the particle. Figure 4.3 shows a typical EPR domain distribution.

![Image](image_url)

**Figure 4.3** Typical distribution of EPR domains in a 15% EPR sample. Scan size is 50 μm.
Scans were performed at different positions within the particle and Figure 4.4 shows the position of the scans. Typical particle diameters are in the range of 500 to 800 μm. Position A was always chosen very close to the edge of the particle and position B was close to the center, typically around 200 to 400 μm from the edge towards the center. AFM images of the 15% EPR sample show distinct domains of EPR distributed in the matrix of length scale on the order of a few hundred nanometers to less than three microns. The images also show a difference in the distribution of EPR domains at different positions within the particle.

Figure 4.5 shows a scan at position A where the EPR domains are closely distributed. Here it can be seen that the domains are separated by a distance on the order of microns or less. Figure 4.6 shows EPR domains near the center of the particle where the EPR domains are of smaller size and are separated by distances larger than those observed in Figure 4.5.
Figure 4.4 Scan positions for images shown in Figure 4.5 and Figure 4.6. Figure not drawn to scale.
**Figure 4.5** Distribution of EPR domains in a 15% EPR sample at scan position A. Scan size is 50 μm.

**Figure 4.6** Distribution of EPR domains in a 15% EPR sample at scan position B. Scan size is 50 μm.
Figure 4.7 shows a higher resolution image where very good contrast between the EPR domains and the polypropylene matrix can be seen. This high-resolution image indicates that EPR domains of different length scales ranging from microns down to a few hundred nanometers exist. This also shows that the distribution of EPR domains is most likely polydisperse. In addition, the shape of the EPR domain cross section is not uniform, although most of the particles can be approximated as circular.
Migration studies

During the actual production of impact copolymer, the polymer particles have been found to agglomerate due to the formation of a sticky substance on the particle surface. This is undesirable since the agglomeration of particles leads to a lower product bulk density and more difficult product handling. Other studies\(^{39}\) have shown that the sticky substance is low molecular weight EPR that migrates to the surface of the polymer. Such migration could influence our surface AFM investigations. In order to study the distribution of EPR domains in the polymer matrix, it is necessary to uncouple the effects due to migration from "normal" EPR distribution. The aim of our migration studies is to use the AFM to observe migration of EPR and develop suitable methods for uncoupling migration effects if the time scales are comparable to the time scales in which the AFM experiments are performed.

Migration studies were performed on a sample prepared at Mitsubishi Chemical Corporation that contained 28.2% EPR and an average EPR molecular weight of 4.48\(\times 10^5\). Force modulation mode with a negative lift of -5 nm was used in this study. The sample was scanned continuously for 12 hours and some of the images are shown in Figure 4.8 to illustrate the migration process.
Figure 4.8 Migration of EPR. Images show the migration of EPR to the surface with time. Scan size is 10 μm.

Figure 4.8 shows a series of images taken at various times after microtoming where the migration of EPR to the surface can be clearly seen. In these, it can be seen that migration is significant at this length scale after approximately three hours of microtoming. The migration studies were also repeated at a different position and at a smaller scan size. But the 'drift' of the scanner was significant at smaller scan lengths and
it shifted the scanned area away from the original scan position making the 5μm scan size results difficult to interpret.

These studies show that migration of EPR is significant only after about 3 hours of microtoming. If AFM studies are therefore performed within 3 hours of microtoming, migration of EPR should not significantly interfere with the experimental observations. All of our studies using AFM were therefore carried out within two hours of microtoming. Though it is possible that EPR migration takes place during the first three hours, the length scale of migrating EPR should be small compared to the EPR domains.
Determination of mass transfer limitations

As discussed in Chapter 1, understanding mass transfer limitations during the copolymerization of ethylene and propylene is key to understanding the growth and distribution of EPR domains within the polypropylene particle. The ability of FM mode to identify EPR domains has been shown previously and therefore can be used to determine if mass transfer limitations exist in the copolymerization reaction.

Figure 4.9 Illustration of the influence of mass transfer limitations on spatial distribution of EPR domains in a polymer particle.
To determine if mass transfer limitations exist, samples with different residence times in the copolymerization reactor were studied. If mass transfer limitations do exist, a gradient in spatial distribution of EPR domains would be observed in samples with decreasing residence times as shown in Figure 4.9. Samples with very low residence times would have more EPR closer to the edge of the particle than at the center if mass transfer limitations do exist. As the residence time increases, more EPR domains would be found deeper inside the particle. However, if there is no appreciable limitation to mass transfer, even particles with a small residence time would have EPR domains evenly distributed throughout the particle.

Samples for mass transfer limitation studies

To study mass transfer limitations, three samples with varying residence times were studied. These samples were prepared under similar conditions but varying residence times and were all approximately 800μm in size. The residence time of each sample is shown in Table 4.1. All samples were prepared with approximately 28% of EPR to uncouple the effect of EPR content from mass transfer limitations.
The samples were first embedded in an epoxy mold and microtomed to generate a flat surface for AFM characterization. All images were scanned within two hours of microtoming to avoid interfering with migrating EPR using force modulation in negative lift mode. A negative lift parameter of $-5$ nm was found to give good contrast between the EPR domains and the polypropylene matrix and was used for all three samples. A scan size of $25 \mu m$ was chosen to minimize scan time and still allow the observation of EPR domains on the order of a few hundred nanometers.

### Table 4.1 Samples used for mass transfer limitation studies.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Residence time (hrs)</th>
<th>EPR content (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q 441</td>
<td>0.33</td>
<td>28.2</td>
</tr>
<tr>
<td>Q 442</td>
<td>1.48</td>
<td>32.6</td>
</tr>
<tr>
<td>Q 447</td>
<td>2.67</td>
<td>28.2</td>
</tr>
</tbody>
</table>
Figure 4.10 AFM image of sample Q441. Scan size is 25μm. Scanned at position A.

Figure 4.11 AFM image of sample Q441. Scan size is 25μm. Scanned at position B.
Figure 4.12 AFM image of sample Q442. Scan size is 25\(\mu\)m. Scanned at position A.

Figure 4.13 AFM image of sample Q442. Scan size is 25\(\mu\)m. Scanned at position B.
Figure 4.14 AFM image of sample Q447. Scan size is 25μm. Scanned at position A.

Figure 4.15 AFM image of sample Q447. Scan size is 25μm. Scanned at position B.
If significant limitations to mass transfer were present, we would expect a gradient in the spatial distribution of EPR domains as we move in from the edge to the center as described earlier. AFM images from samples with increasing residence times however show EPR domains at the edge as well as the center.

From the images, one can observe that morphology of EPR domains near the edge of the particle approaches that of a continuous morphology while EPR domains near the center appear discrete in all three samples. In addition, EPR domain size increases with time. Even in the sample with the shortest residence time, EPR domains are observed near the center, the size of which increases with increasing residence time. This indicates the absence of any significant limitations to mass transfer.

Our studies indicate atomic force microscopy is a powerful tool to investigate morphology development in PP-EPR composites. We have been able to identify EPR domains and study their distribution within the polypropylene matrix. Migration studies were performed to determine the time scales of EPR migration. Mass transfer limitation studies indicate the absence of significant limitations to mass transfer during copolymerization.
Chapter 5

MORPHOLOGY CHARACTERIZATION USING

SMALL ANGLE LIGHT SCATTERING

Small angle light scattering (SALS) was used to characterize the bulk morphology of the PP-EPR copolymer composite. The aim of our SALS studies is to characterize and understand morphology development during the domain growth process. As before, preliminary studies were first carried out to establish proper methodology to conduct our investigations.

Initial studies

The purpose of our initial studies was to establish the appropriate models required for the analysis of SALS data from high impact polypropylene. Initial studies were performed on samples containing 5% and 15% EPR and the melt squash method described earlier was used to prepare the samples. Scattering data was collected as described in Chapter 3, then transferred to Igor Pro and radially averaged to get the intensity-wave vector relationship. Scattering curves from the 5% EPR and the 15% EPR samples are shown in Figure 5.1.
The data was first fit using a model that assumes EPR domains are monodisperse and spherical in shape (Equation 3.6, Chapter 3). The fit of this model to data for the 15% EPR sample is shown in Figure 5.2. Here it can be seen that this model is a poor fit and indicates that the EPR domains may not be spherical and that the distribution of EPR is likely not monodisperse. It is a reasonable and probably necessary approximation to consider the particles to be spherical in shape since the exact shape of the particles is not known. AFM images shown previously (e.g. Figure 4.5 in Chapter 4) indicate that the average particle resembles a sphere and that the EPR domains are not monodisperse.
These images as well as the poor fit using the simple model indicate that we must use a model that incorporates polydispersity.

**Figure 5.2** Scattering data for 15% EPR sample and fit to a simple scattering model for monodisperse spheres.
Incorporating polydispersity - The Schulz model

As supported by the AFM studies and initial SALS studies, the EPR domains are not monodisperse. It is therefore necessary to use a light scattering model that incorporates polydispersity. The Schulz model\(^40\) is a commonly used model for polydisperse systems:

\[
f(a) = (z + 1)^z + 1 \cdot x^z \frac{\exp(-(z + 1)x)}{\bar{a} \Gamma(z + 1)}
\]  

(5.1)

where \(f(a)\) 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.

Assuming this distribution, an analytical expression has been derived\(^41\) for the form factor of spherical scattering particles:

\[
P(q) = \frac{9}{2 z_1 q^6} \left\{ z_1 \left[ 1 - \frac{\cos(z_1 w)}{(1 + 4 u^2)^{s_1 / 2}} - \frac{2 q \sin(z_1 w)}{(1 + 4 u^2)^{s_2 / 2}} \right] + q^2 z_2 \left[ 1 + \frac{\cos(z_2 w)}{(1 + 4 u^2)^{s_1 / 2}} \right] \right\}
\]  

(5.2)
where
\[ u = \frac{q}{z_i}, \]
\[ \omega = \arctan(2u), \]
\[ z_j = z + j. \]

Assuming no interactions between EPR domains, \( I(q) = P(q) \) and the light scattering data can be fit to this analytical expression for the form factor. From this fit, parameters \( z \) and \( a \) are used to obtain the number-normalized EPR domain size distribution \( F_N(a) \) (using Equation 5.1). Since smaller particles have less EPR than large particles, this number distribution is converted to a volume-normalized distribution \( F_v(a) \) which provides an effective volume fraction distribution of the EPR domains of a given size in the sample.

The number distribution is converted to a volume-normalized distribution by:

\[
F_v(a) = \frac{V(a)F_N(a)}{\int F_N(a)V(a)\,da}
\]

where \( V(a) = \frac{4}{3} \pi a^3 \)

Figure 5.3 shows the fit to a Schulz model for a 15% EPR sample where the model gives a much better fit and a measure of the size distribution over a wider \( q \) range than the simple monodisperse model. Figures 5.4 and 5.5 illustrate EPR domain size number and volume distributions for 5% EPR and 15% EPR samples. Since the 15% EPR sample contains 3 times the volume of EPR as the 5% EPR sample, the volume
normalized distribution of the 15% EPR sample was multiplied by 3 in order to compare with the 5% EPR sample. The distributions indicate an increase in the number of smaller domains in the sample with 15% EPR content. The model works well for both samples used for our initial studies.

Figure 5.3 Scattering data for 15% EPR sample and fit to Schulz model.
**Figure 5.4** Number-normalized size distribution of 5% and 15% EPR obtained from a Schulz model fit. Solid line represents 15% EPR and dashed line represents 5% EPR.

**Figure 5.5** Volume-normalized size distribution of 5% and 15% EPR obtained from a Schulz model fit. Solid line represents 15% EPR and dashed line represents 5% EPR.
SALS studies on a concentration series

The aim of our studies on the concentration series is to investigate and understand morphology development of EPR domains during the domain growth process. SALS experiments were conducted to observe any transition in morphology as the amount of EPR increases. Samples with EPR contents ranging from approximately 5% to approximately 25% were studied. The samples were classified as low (L), medium (M) and high (H) depending on their EPR content as shown in Table 5.1

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>EPR content wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1-L3</td>
<td>5% to 10%</td>
</tr>
<tr>
<td>M1-M3</td>
<td>10% to 16%</td>
</tr>
<tr>
<td>H1</td>
<td>&gt;16%</td>
</tr>
</tbody>
</table>

Table 5.1 Samples studied using small angle light scattering.
The samples for these SALS studies were prepared using the 'melt-squash' approach described previously in Chapter 3. Data was collected from four different regions of the sample, averaged and then repeated to confirm the consistency of the observed data. The scattering data was subsequently analyzed and fit to the Schulz model.

Figure 5.6 Scattering curves for the concentration series. Scattering data for pure polypropylene is also shown.
Background scattering

Background scattering has to be subtracted from the observed data to minimize scattering that might occur from sources other than the EPR domains. The scattering curve from pure polypropylene is shown in Figure 5.6 where its magnitude is greater than the composite samples. We believe that scattering in the pure polypropylene case arises from spherulites that can form during the sample preparation by the melt-squash method but do not appear in the composites. Hence a background only from the index-matching solvent was subtracted.

Bimodal Schulz distribution

Though used before for polydisperse systems, the Schulz model does not fit the data very well. AFM studies (for example, Figure 4.5 and Figure 4.6) indicate that the EPR domain distribution is spread over two different size ranges. The scattering curves for samples with low and medium EPR content also show a shift in the slope at lower $q$ suggesting that the distribution may be spread over two different size ranges. Hence the Schulz model was modified to accommodate a bimodal distribution of particles.
This was done by considering the Schulz model to be a sum of two distributions:

$$f(a_1, a_2) = \frac{A_1 f(a_1) + A_2 f(a_2)}{A_1 + A_2}$$

$$= \left\{ \begin{array}{l}
\frac{A_1}{(A_1 + A_2)} (z_1 + 1)z_1 + 1 x_1 z_1 \exp \left( -\frac{(z_1 + 1)x_1}{\bar{a}\Gamma(z_1 + 1)} \right) \\
+ \frac{A_2}{(A_1 + A_2)} (z_2 + 1)z_2 + 1 x_2 z_2 \exp \left( -\frac{(z_2 + 1)x_2}{\bar{a}\Gamma(z_2 + 1)} \right)
\end{array} \right. \quad (5.3)$$

where the subscripts 1 and 2 represent two different distributions and

$$\frac{A_1}{(A_1 + A_2)} \quad \text{and} \quad \frac{A_2}{(A_1 + A_2)}$$

represent the fractional contribution of each individual distribution. The form factor is now given in terms of $A_1$ and $A_2$ as

$$P(q) = \begin{cases} 
\frac{A_1}{(A_1 + A_2)} 9 z_{a_1} \left\{ \begin{array}{l}
1 - \frac{\cos(z_{a_1} w_{a_1})}{(1 + 4u_{a_1}^2)^{z_{a_1}/2}} - \frac{2q_{a_1} \sin(z_{a_1} w_{a_1})}{(1 + 4u_{a_1}^2)^{z_{a_1}/2}} \\
+ q_{a_1}^2 z_{a_1} \left\{ 1 + \frac{\cos(z_{a_1} w_{a_1})}{(1 + 4u_{a_1}^2)^{z_{a_1}/2}} \right\}
\end{array} \right. \\
+ \frac{A_2}{(A_1 + A_2)} 9 z_{a_2} \left\{ \begin{array}{l}
1 - \frac{\cos(z_{a_2} w_{a_2})}{(1 + 4u_{a_2}^2)^{z_{a_2}/2}} - \frac{2q_{a_2} \sin(z_{a_2} w_{a_2})}{(1 + 4u_{a_2}^2)^{z_{a_2}/2}} \\
+ q_{a_2}^2 z_{a_2} \left\{ 1 + \frac{\cos(z_{a_2} w_{a_2})}{(1 + 4u_{a_2}^2)^{z_{a_2}/2}} \right\}
\end{array} \right. \end{cases} \quad (5.4)$$
where

\( a_1, a_2 \) represent two different size

\[ u = q / z, \]
\[ w = \arctan(2u), \]

\[ z_{a,i,j} = z_{a,i} + j. \]

The bimodal Schulz model fits light scattering data over a wide range of \( q \) very well as shown in Figure 5.7. The fit parameters are tabulated in Table 5.2.
The scattering curves for the samples with low and medium EPR content are similar in shape, indicating the morphology in these samples are similar. However, the curve for the sample with high EPR content is very different from the other samples indicating that this sample has a very different morphology from the other samples. This is confirmed in Figure 5.8 where the volume-normalized distributions for the samples are shown. Here it can be seen that the distribution for the high EPR content sample is shifted towards very large particle sizes suggesting the morphology in this sample may be bicontinuous.

![Figure 5.7 Scattering data and fit to bimodal Schulz model.](image)

**Figure 5.7** Scattering data and fit to bimodal Schulz model.
<table>
<thead>
<tr>
<th>Sample</th>
<th>EPR classification</th>
<th>Schulz model fit parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$a_1$ nm.</td>
</tr>
<tr>
<td>L-1</td>
<td>Low (5%-10%)</td>
<td>1370</td>
</tr>
<tr>
<td>L-3</td>
<td>Low (5%-10%)</td>
<td>1392</td>
</tr>
<tr>
<td>L-4</td>
<td>Low (5%-10%)</td>
<td>1627</td>
</tr>
<tr>
<td>M-1</td>
<td>Medium (10%-16%)</td>
<td>1667</td>
</tr>
<tr>
<td>M-2</td>
<td>Medium (10%-16%)</td>
<td>1453</td>
</tr>
<tr>
<td>M-3</td>
<td>Medium (10%-16%)</td>
<td>1858</td>
</tr>
<tr>
<td>H-1</td>
<td>High (&gt;16%)</td>
<td>7101</td>
</tr>
</tbody>
</table>

Table 5.2 Schulz model fit parameters to concentration series.
For the high EPR content sample, a different method of analysis was performed to confirm our observation that the morphology may be bicontinuous. The Debye-Bueche model\textsuperscript{42} was used to analyze the scattering data. This model is commonly used to fit scattering data from bicontinuous systems\textsuperscript{43}. In simplified terms, the model can be expressed as

\[ I(q) = \frac{I(0)}{(1 + q^2a_c^2)^{-2}} \]
where \( a_c \) is the correlation length. A plot of \( I(q)^{1/2} \) vs. \( q^2 \), 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 5.9.

\[ I(q)^{1/2} \sim q^2 \]

Figure 5.9 Debye-Bueche plot showing the applicability of Debye-Bueche model indicating bicontinuous morphology.

The linear fit at low \( q \) to a Debye-Bueche plot indicates that morphology in the high EPR case resembles a bicontinuous morphology. The fit is linear only at low \( q \) corresponding to larger domain sizes probably indicating the presence of discrete domains of smaller length scales. The scattering data also indicates a clear change in
morphology in this sample and the Schulz distribution also indicates a shift towards very large domain size. These observations lead to the conclusion that the morphology is shifting towards that of a bicontinuous morphology at high EPR concentrations.

To verify this conclusion, AFM studies were made on the sample with high EPR content. The AFM image of this sample is shown in Figure 5.10 where the image indicates that the morphology is indeed shifting towards that of a bicontinuous morphology, confirming the SALS observations.

![AFM image of sample H1 indicating a bicontinuous morphology. Scan size is 25 μm.](image)

**Figure 5.10** AFM image of sample H1 indicating a bicontinuous morphology. Scan size is 25 μm.
This work indicates that SALS is a very useful tool in characterizing the size and distribution of EPR domains in the PP-EPR system. Size and distribution for a series of EPR concentrations were measured and indicate that the morphology of EPR domains is shifting towards that of a bicontinuous morphology as concentration is increased. This observation is also supported by our AFM investigations.
Chapter 6

CONCLUSIONS

The morphology of high impact polypropylene was characterized using atomic force microscopy (AFM) and small angle light scattering (SALS). AFM was used to study distribution of EPR domains in the polypropylene matrix and SALS was used to study EPR domain size distribution and EPR domain morphology development.

Atomic force microscopy studies

It has been shown that AFM is a useful tool in identifying EPR domains in a polypropylene matrix. Our studies show that EPR domains are distinct in samples containing less than 15% EPR and that the morphology shifts towards that of a bicontinuous network when the EPR content is increased to approximately 30%.

Migration of EPR to the surface of the polymer was also observed with the AFM. It is clear that EPR migrates to the surface but significant migration was observed only three hours after creating the surface. The AFM was also used to determine if any
limitations to mass transfer exist during EPR polymerization. Studies were performed on samples with different residence times and it was found that EPR was present throughout the PP particle. The EPR domain size was also found to increase with residence time. These observations indicate that mass transfer limitations may not be significant during EPR polymerization at overall low EPR contents.

Small angle light scattering studies

SALS was used to study the morphology development of EPR domains. To do so, samples containing increasing EPR content were studied and SALS clearly indicates a significant change in morphology with increasing EPR content. Light scattering models were developed to provide information on both EPR domain sizes as well as size distribution. It was found that the length scales obtained from SALS are comparable to those from AFM measurements.

Recommendations for further studies

AFM and SALS studies have provided useful information about the morphology of high impact polypropylene. The AFM has shown that the morphology of EPR domains changes with EPR content. A systematic study of samples with increasing EPR content from medium to high concentrations would clearly indicate the onset of the morphological transition to a bicontinuous morphology. AFM images show that
migration of EPR is significant only after 3 hours of creating a surface. Migration studies using a different approach may provide information about migration in the first few hours. For example, EPR at the surface may be dissolved into solution using a suitable solvent and the amount of EPR in the solution may be analyzed to determine the significance of migration in the first few hours after creation of new surface.

Mass transfer studies indicate no significant limitation to mass transfer. These observations could be confirmed by performing similar studies on samples with different particle sizes. Studies performed on samples with higher EPR content will help establish the effect of EPR content on mass transfer limitation.

SALS studies have indicated a change in morphology as the EPR content is increased from low to high. SALS studies performed on samples with small increments of EPR content from medium to high would clearly establish at what point the morphology changes from a distinct to a bicontinuous two-phase morphology. In addition, the light scattering apparatus can be modified to observe a wider range of $q$ to provide more information about larger and smaller EPR domains. Information about larger domains can be obtained by modifying the set up to observe scattering at lower $q$ by increasing the distance between sample stage and detector. By expanding the set up to include wider angles, information about smaller domains can be obtained. A better
description of the shape of EPR domains may be used to obtain more accurate information about domain size distribution from scattering.
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