



# In-situ spectroscopic and thermal analyses of phase domains in high-impact polypropylene

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## ABSTRACT

High-impact polypropylene (HIPP) is a commercially important polymer alloy with complex morphological structure. In this contribution, two commercial HIPPs have been investigated in detail by atomic force microscopy-infrared in conjunction with local thermal analysis to determine the composition and structure of the nanodomains. Both alloys contain numerous core-shell rubber particles dispersed in polypropylene matrix. In HIPP-1, the rigid cores of the particles are rich in polypropylene, which is highly crystalline, whereas for HIPP-2, the major component of the rigid cores is polyethylene with a high degree of crystallinity. The formation of these very different structures and compositions in the core and rubber domains may be attributed to different chain structures and compositions of the copolymers in the alloys produced by different catalysts.

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## 1. Introduction

Polypropylene (PP), due to its many valuable properties, such as high tensile strength, outstanding thermal resistance, processability and low production cost, is one of the most important and widely used commercial polymers in the world since its introduction into the global market in 1950s [1,2]. These advantages also make PP versatile for some special applications, such as films and containers in food packaging and medical devices [3,4]. However, PP is brittle, especially at low temperatures and high speed, and in past several decades various approaches have been developed to improve its toughness, such as blending with some elastomers [5–7], rigid polymers [8] and inorganic particles [9,10], and introduction of submicrometer voids into PP matrix [11]. The properties of these blends are not satisfactory due to poor compatibility between the components, and more recently, a new method to synthesize PP copolymers with multi-phase microstructure in reactor by copolymerization with other olefinic species, usually ethylene, was introduced [12–14]. By using porous Ziegler-Natta (Z-N) based

catalyst in a multistage polymerization process, which includes bulk polymerization of propylene in the first stage and copolymerization of propylene and ethylene in the second stage, the rubber phase is formed in the isotactic PP (iPP) primary particles directly, leading to a much higher degree of distribution of the rubber phase in PP than in blends prepared by mechanical blending [15–19]. These PP in-reactor alloys, often called high-impact polypropylene (HIPP) or impact polypropylene copolymer (IPC), offer superior stiffness and impact resistance balance and have found extensive application in various fields.

It is well believed that the superior mechanical properties of HIPP originate from its complicated composition and phase structure, and extensive research has been carried out in order to understand and optimize the composition and structure and hence the performance of HIPP. Thermal analysis and spectroscopic techniques, such as differential scanning calorimetry (DSC), NMR and FT-IR, in conjunction with solvent/thermal fractionation methods, including temperature rising elution fractionation, temperature gradient extraction fractionation, crystallization analysis fractionation and high temperature solvent gradient interaction chromatography, have revealed in HIPP the presence of ethylene-propylene random copolymer (also called ethylene-propylene rubber, EPR) and ethylene-propylene block copolymers (E-b-P), in

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addition to PP and possibly a small amount of polyethylene (PE) homopolymers [20–27]. The content, molecular weight and exact structure of each component depend on specific polymerization conditions. Then, by using various microscopic techniques, including scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM), assisted by selective solvent etching and selective staining, the components are found to form complex multilevel phase structures, typically consisting of core-shell rubber particles dispersed in an *i*PP matrix [20,24,28–30]. The presence of rigid cores in the rubber particles is the key to the balance between toughness and stiffness of HIPP [31,32]. In-depth studies have established that the soft intermediate layer between the rigid cores and the matrix is made up of EPR. However, the composition of the rigid cores remains controversial, and various models with a PE-rich core composing either crystalline PE homopolymers or PE-rich *E-b*-Ps or both have been proposed mainly on the basis of TEM and selected area electron diffraction (SAED) findings [30,32–34]. More recently, it was revealed that the rigid cores in some commercial HIPPs could be PP-rich as well [35]. One key reason for this is lack of in-situ and direct method for analyzing the composition and structure of the nano domains in the HIPP. More specifically, electron microscopic techniques such as SEM and TEM cannot differentiate *i*PP, PE and *E-b*-P phases unambiguously or quantify the domain composition. On the other hand, fractionation methods combined with other analytical techniques do provide rich information on the composition and chain structure of the different HIPP components, but the original phase structure is destroyed in the fractionation process and the corresponding location information for the components is lost.

A recently emerged technique, AFM-IR, opens a new avenue of direct investigation of domain composition and structure in situ for HIPP [35]. The novel technique, based on the photo-thermal induced resonance (PTIR) effect, has increased the spatial resolution of IR spectroscopy to sub-100 nm scale [36,37]. Fig. S1a (Supporting Information) illustrates the contact model AFM-IR setup built around an AFM and a tunable pulsed infrared laser. The thin film sample is illuminated by monochromatic IR pulses, through a total internal reflection crystal in the present case, and local absorption of the infrared at this particular wavelength results in heating and thermal expansion of the sample, which is detected by the AFM tip placed on the sample surface. By measuring the AFM cantilever oscillation amplitude as a function of the IR wavelength, an AFM-IR spectrum is obtained. In the novel design, the AFM tip acts as a “spatial filter” allowing the collection of IR spectra with nanoscale spatial resolution, many times smaller than that of conventional FT-IR. The technique thus combines the chemical analysis capability of IR spectroscopy with the spatial resolution of AFM, and provides a powerful tool for studying microstructure and chemical composition of a diverse range of materials, including polymers [38], semiconductors [39], quantum dots [40], solar energy materials [41], bio-matters [42,43], cells [44], microorganisms [45], pharmaceutical blends [46,47], metal organic frameworks (MOF) [48], even monitoring photocatalysis [49] and amyloid formation [50], and confirming the Eoarchean life elements trapped in mineral inclusions [51].

In a recent work, for the first time we demonstrated that AFM-IR can be employed for quantitative analysis of nanodomain composition in polymer systems, and by using this new method we also discovered that PP can be the major component of the rigid cores in a commercial HIPP sample, which is contrary to that previously believed [35]. In an attempt to clarify this issue, in the present study, composition and morphological structure of different domains of two commercial HIPPs produced using different types of Z-N catalyst are investigated by utilizing AFM-IR and another newly

developed technique, local thermal analysis (LTA). We show that the major component of the rigid cores indeed can be either PP or PE, with significant degree of crystallinity.

## 2. Experimental section

### 2.1. Materials

PP and PE homopolymers and two HIPP samples synthesized with different Z-N catalysts were all commercial products provided by ExxonMobil in the form of injection molded disks.

### 2.2. Microscopy

HIPP samples were microtomed into thin sections by cryo-microtomy performed at  $-120^{\circ}\text{C}$  with a RMC PowerTome™ XL cryo-microtome system and stained overnight with  $\text{RuO}_4$  prepared in-situ (by oxidizing ruthenium chloride hydrate with sodium hypochlorite). Then high angle annular dark field scanning transmission electron microscopic (HAADF-STEM) images were collected on a FEI Tecnai F20 ST microscope. Tapping mode AFM images were collected at a resolution of  $512 \times 512$  on a Bruker Dimension Icon system after the samples were cross-sectioned by microtomy at  $-140^{\circ}\text{C}$  with a Leica EM-UC7 ultramicrotome system equipped with a Leica EM FC7 cryo-chamber.

### 2.3. Composition analysis

Domain composition for the HIPP samples was analyzed following a method reported previously [35]. In brief, a HIPP thin film of  $\sim 200$ – $400$  nm thickness (tested by contact mode AFM), prepared using a Leica microtome, was placed on a ZnSe prism of a nanoIR unit (Anasys Instruments), and an AFM image was acquired in contact mode using an EX-C450 tip (Anasys Instruments) to identify the morphology. Then the sample was illuminated from underneath by total internal reflection with a Ekspla optical parametric oscillator laser with a  $900$ – $2000\text{ cm}^{-1}$  tuning range and a spectral resolution of  $4\text{ cm}^{-1}$ . AFM-IR spectra were generated by measuring the thermal expansion of the sample with the AFM tip as a function of the IR laser wavelength normalized by the laser intensity averaged over 128 pulses. A calibration was established based on FT-IR spectra of ethylene-propylene copolymers with known compositions, acquired on a Nicolet 6700 spectrometer equipped with a MCT detector and an ATR accessory (ZnSe crystal,  $45^{\circ}$ , Pike Technologies), and was employed to convert the peak ratios in the AFM-IR spectra into composition ratios.

### 2.4. Spectroscopic analysis and IR imaging

A thin film of  $\sim 100$ – $300$  nm thickness was attached onto a smooth silicon wafer surface tightly, and analyzed using a nanoIR2-FS™ system (Anasys Instruments). First, tapping mode AFM images were collected at a  $300 \times 300$  spatial resolution to identify the nano domains, and then AFM-IR spectra in the  $1500$ – $900\text{ cm}^{-1}$  region were collected using a quantum cascade laser as illumination tuned to match the resonance of the AFM cantilever in order to achieve maximum sensitivity. The data were recorded at  $2\text{ cm}^{-1}$  spacing and averaged and smoothed using a Savitzky-Golay filter. IR images were acquired by scanning the AFM tip across the sample at a specific IR wavelength in tapping mode operation. For each spectral point and each pixel of the IR image  $\sim 300$ – $600$  pulses were accumulated based on the lock-in time constant.

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