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Short communication

Nanoscale chemical imaging of a deuterium-labeled polyolefin copolymer in a polyolefin blend by atomic force microscopy-infrared spectroscopy

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ABSTRACT

A combination of atomic force microscopy-infrared spectroscopy (AFM-IR) and a deuterium-labeled ethylene-propylene (EP) copolymer enables direct nanoscale chemical imaging of all three components in a polyethylene/polypropylene/ethylene-propylene copolymer blend for the first time. AFM-IR is a hybrid technique that provides the spatial resolution of AFM with the chemical selectivity of IR. Deuterium labeling of the EP copolymer enables it to be distinguished from the blend components. This combination enables chemical imaging of all components in the polyolefin blend at a spatial resolution (~50 nm) that far exceeds conventional Fourier-transform infrared and Raman microscopy, which are limited by the diffraction of light. AFM-IR spectra and images of the C-D stretch in the polyolefin blend definitively establish that the deuterium-labeled EP copolymer is dispersed in the polyethylene matrix. This strategy is broadly applicable to other types of polymer blends that contain chemically-similar components.

1. Introduction

Plastic waste streams often contain both polyethylene (E) and polypropylene (P). These polymers are immiscible, and as a result, it is difficult to obtain satisfactory physical properties without a compatibilizing polymer. In this report, an experimental ethylene-propylene (EP) copolymer was used to compatibilize blends of E and P.

Phase size is one measure of the effectiveness of the EP copolymer in the E and P blend [1], but with traditional imaging techniques, it is difficult to determine if the EP copolymer prefers one phase or the other because the composition of the copolymer is similar to E and P. Deuterium labeling of the EP copolymer enables it to be distinguished from the blend components. Furthermore, deuterium labeling is a small perturbation of the polymer's structure that does not affect the thermodynamics of blends for the modest molecular weights and deuterium concentration considered here [2,3]. Fourier-transform infrared (FTIR) [4] and Raman [5–7] microscopy of polymer blends with deuterium-labeled components have been reported in the literature. However, the spatial resolutions of FTIR and Raman microscopy are limited by the diffraction of light to ~10 μm and ~1 μm, respectively. A much higher spatial resolution (i.e., <100 nm) is required to characterize phase-separated materials with small domains and to observe the interface between each phase.

Atomic force microscopy coupled to infrared spectroscopy (AFM-IR) is a hybrid technique that combines the spatial resolution of AFM with the chemical selectivity of IR [8]. Briefly, the method uses an AFM tip to detect the IR absorption in the contact area under the tip due to the photothermal effect. AFM-IR spectra can be acquired at a single point by scanning the wavelength of a pulsed mid-IR laser, and AFM-IR mapping can be obtained by scanning a field of view at a fixed wavelength. AFM-IR provides nanoscale chemical imaging at a spatial resolution that is better than 50 nm, but it is not able to distinguish the EP copolymer from E and P. A

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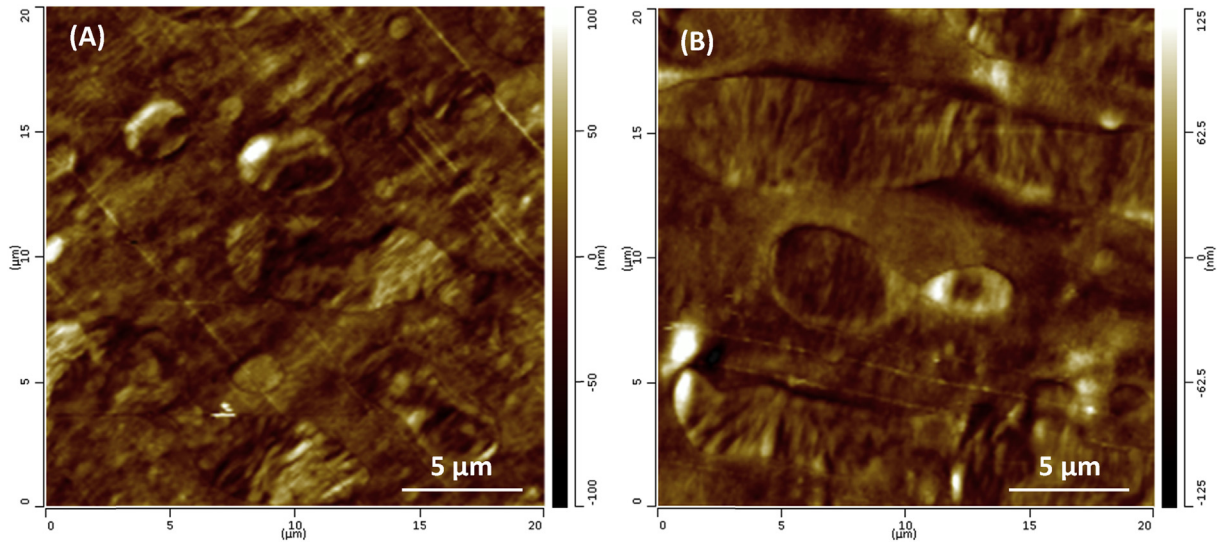

Fig. 1. AFM height images of the **(A)** E/P/EP blend and **(B)** E/P/dEP blend.

combination of AFM-IR and a deuterium-labeled EP copolymer enables direct nanoscale chemical imaging of all three components in the polyolefin blend for the first time. This strategy is broadly applicable to other types of polymer blends that contain chemically-similar components.

2. Experimental methods

Deuterium exchange of an ethylene-propylene copolymer was accomplished using literature methods [9,10]. 3.0 g of the copolymer was combined with 1.0 g of a Pt-Re/SiO_2 catalyst and 270 mL of 2,2,4-trimethylpentane in a sealed 600 mL reactor. The reaction was carried out under 600 psi of D_2 at 170 °C for 16 h. Following the reaction, the solvent was evaporated, and the polymer/catalyst was redissolved in 1,2,4-trichlorobenzene (TCB) at 150 °C and filtered using pearlite. The polymer was recovered by precipitating the filtrate in cold methanol then drying in a vacuum oven at 60 °C for 72 h. The exchange yield (by moles), as measured by ^{1}H NMR, was 0.30.

A predominately ethylenic polymer (E), predominately propylenic polymer (P), and the ethylene-propylene copolymer (EP) were solution blended by first dissolving the components in TCB at 150 °C in a 64/27/9 (E/P/EP) mass ratio. Corresponding blends were made using the deuterium-labeled ethylene-propylene copolymer (dEP). The solutions were precipitated into methanol, rinsed, and then dried in a vacuum oven at 60 °C for 72 h. The recovered materials were compression molded into films at 190 °C.

AFM samples were prepared as 300 nm thin sections by cryomicrotomy (−100 °C, Leica) and placed on gold mirrors (Thorlabs, Inc.). AFM-IR data were collected with a NanoIR2 instrument from

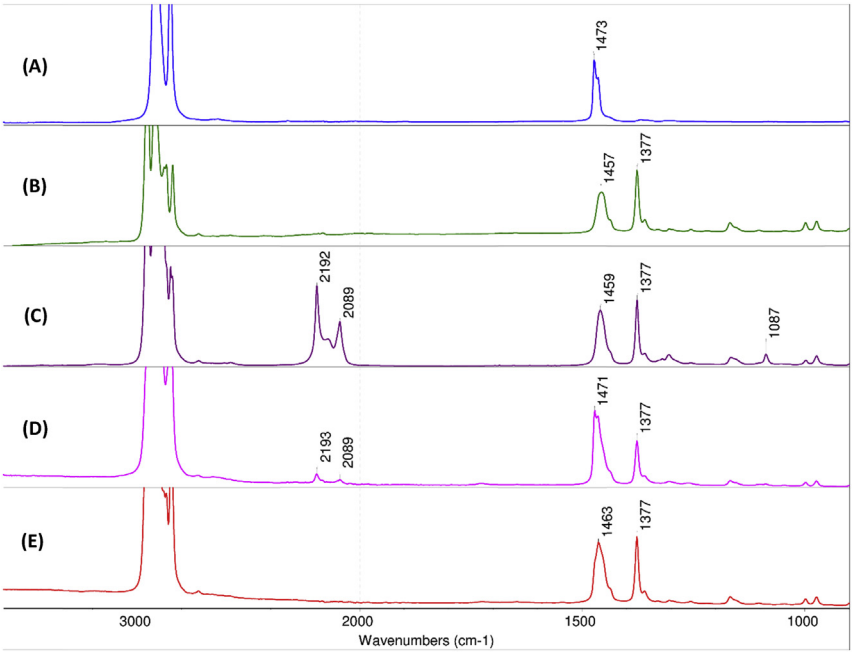

Fig. 2. Bulk FTIR spectra of **(A)** E, **(B)** P, **(C)** dEP, **(D)** E/P/dEP copolymer blend, and **(E)** E/P/EP copolymer blend. The spectra are shown in absorbance.