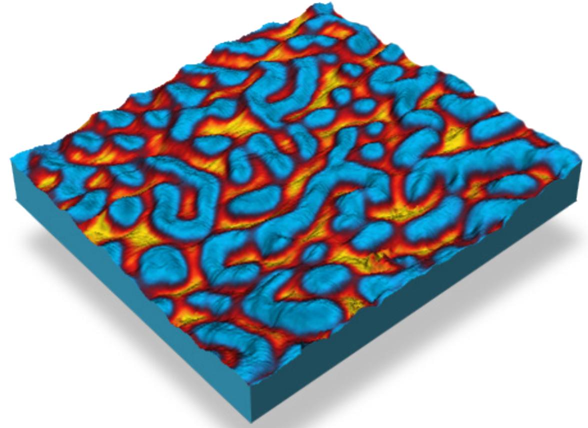
Achieve a deeper understanding of polymeric systems

- nanoIR spectroscopy uniquely and unambiguously identifies the chemical composition of polymeric thin films and multilayer structures
- Tapping AFM-IR provides <10 nm chemical mapping spatial resolution with simultaneous mechanical property mapping
- nanoscale IR spec troscopy directly correlates to bulk FTIR libraries for easy material identification



PS/PMMA blend chemical contrast image

Abstract

This note describes the application of the nanoIR2-FS™ system to the chemical characterization of a range of polymeric materials and structures. The nanoIR2-FS system is based on a scientific breakthrough technique of acquiring IR spectra at spatial resolutions well below the diffraction limit of conventional IR spectroscopy, enabling researchers to obtain nanoscale chemical fingerprints of their material. The spectra generated using Anasys Instruments' patented **AFM-IR**™ technique directly correlate with traditional FTIR spectra, and are thus searchable in standard FTIR databases. In addition to chemical analysis, the nanoIR2-FS provides the ability to probe mechanical, thermal, and topographical properties of samples with nanoscale spatial resolution.

Key words

Submicron IR spectroscopy | Multilayer films | Food packaging

Introduction

Infrared (IR) spectroscopy is one of the most recognized analytical measurement techniques in academic, government, and industrial R&D laboratories for the characterization of polymeric materials. The spatial resolution of conventional bulk IR spectroscopy is limited by Abbe diffraction laws to between 3 – 10 µm, depending on the method used. Atomic Force Microscopy (AFM) is a widely used nanoscale imaging technique that provides the user with a high spatial resolution topographic map of a sample surface.

Until now, the major drawback of AFM has been its inability to chemically characterize the material underneath the tip. When combined with an IR source; the resulting AFM-IR technique breaks the diffraction limit of conventional IR spectroscopy by orders of magnitude, while still providing the high resolution imaging capabilities of AFM.1

In this note, we will discuss the use of AFM-IR to address nanoscale chemical characterization on a range of polymeric samples.

Characterization of multilayer films

Multilayer films are of great importance in many products, especially packaging materials. As multilayer films become thinner and the number of individual layers increases, there is a need to characterize these structures[2]. FTIR spectroscopy is widely used for characterizing cross sections of multilayer films, providing information about the chemical nature of the individual polymers layers, as long as they are at least a few micrometers thick. Previously, in order to analyze individual layers that are smaller than the diffraction limit of conventional FTIR, films had to be delaminated. AFM-IR is able to overcome these obstacles, and thus can provide true nanoscale chemical characterization.

To reverse engineer multilayer films, samples are cross sectioned by microtome and are placed on an IR transparent substrate (ZnS) for analysis, shown in figure 1a. Subsequent AFM-IR spectra are denoted by the respectively colored markers; in this case, as can be seen in figure 1b and 1c, the contents of the film were successfully identified as polyethylene and polyamide .

Each layer within multilayer films can have a specific function, such as oxygen or moisture barrier layers. It is very common for these materials to be incompatible with one another and as a result, "tie" layers are needed to bind these layers together during film formation. Until now, it has been impossible to characterize these tie layers by FTIR spectroscopy due to their thickness (<500 nm).

Such an example is the relationship between polyethylene (PE) and polyamide (PA). These polymers are not compatible within films, and a tie layer is generally required. Figure 2 shows an AFM height image and AFM-IR spectra from the boundary region between the PE and PA layer of a cling film cross section. The nine colored marker locations on the AFM image correspond with the AFM-IR spectra of the same color (100 nm spacing).

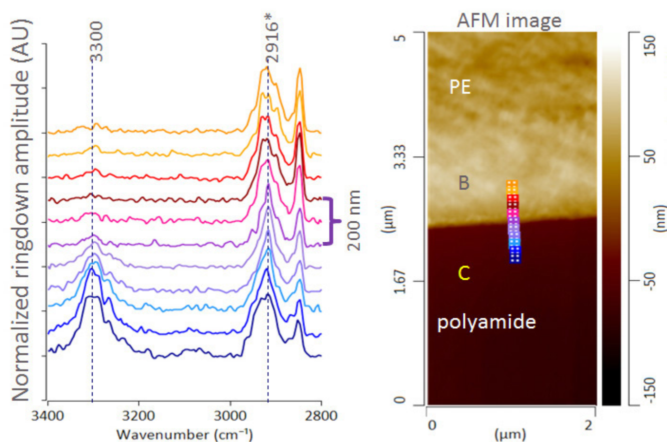


Figure 2: AFM height image and AFM-IR spectra across PE/PA layer interface

The spectra recorded within 200 nm of the boundary have significantly sharper CH2-stretching bands than the areas of the PE further away from the boundary. Furthermore, the center-of-mass peak wavenumber of the CH2 antisymmetric stretching band also shifts to lower wavenumber (2916 cm^{-1}) at the boundary, suggesting more ordered hydrocarbon and less branched chains. This means, for the first time, the tie layers between polymers can be accurately chemically characterized.

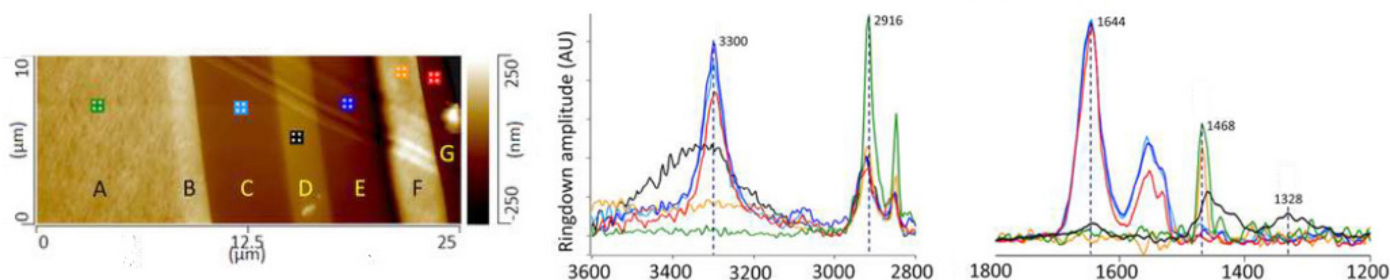


Figure 1: (a) AFM height image showing cross sectioned multilayer film. AFM-IR spectra at 2800-3600 cm^{-1} (b) and 1200-1800 cm^{-1} (c); spectra collected from layers C, E, and G are consistent with a polyamide. The IR spectrum recorded from layer D, which can be considered as the barrier layer in the film, is consistent with polyethylene-co-(vinyl alcohol) (EVOH)

Measuring monolayers

Self-assembled monolayers (SAMs) of 4-nitrothiophenol (NTP) and a monolayer island sample of poly(ethylene glycol) methyl ether thiol (PEG) were deposited on template-stripped gold substrates. AFM topography measurements were used to verify that the NTP monolayer film thickness was less than 1 nm, as shown in figure 3a. AFM-IR spectra and molecular structures of NTP SAMs on gold (in blue) as shown in figure 3. Each AFM-IR spectrum originates from an approximate sample surface area of 25 nm × 25 nm, limited only by the contact area of the AFM probe with the sample[3].

Corresponding IR reflection absorption spectra recorded over a substantially larger area of NTP SAMs are shown in red for comparison, shown in figure 3c. A strong NTP absorption peak around 1339 cm^{-1} correlates to the symmetric NO2 stretching mode, while the weaker absorption band around 1175 cm^{-1} is associated with an aromatic CH-bending mode. An array of AFM-IR spectra were collected across a gap in the monolayer as shown in figure 3c. The spatial resolution achieved for these measurements was ~20 nm.

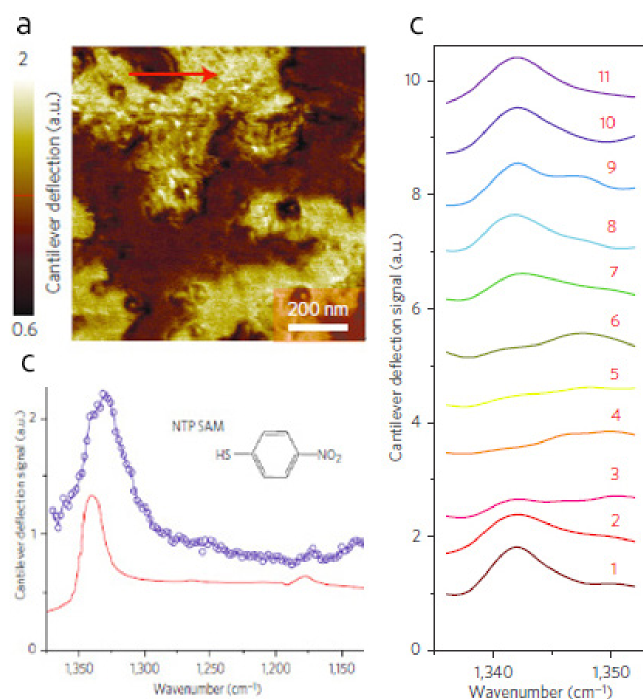


Figure 3: (a) AFM deflection image showing SAM's of NTP on gold substrate. (b) Comparison of AFM-IR spectrum (blue) and ATR spectrum (red) of NTP SAM's. (c) Array of AFM-IR spectra collected across red line shown in (a) demonstrating spatial resolutions of ~20 nm

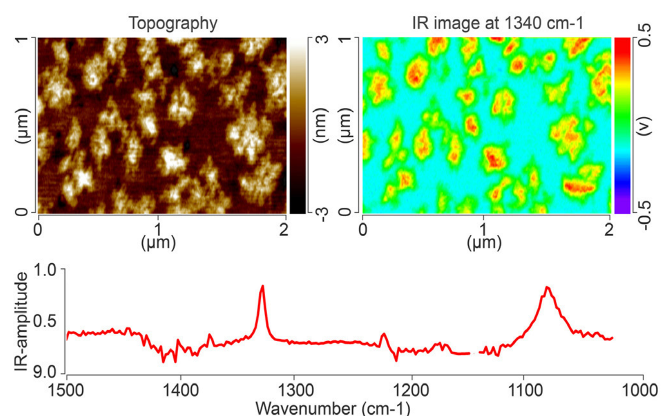


Figure 4: AFM topography image (top left), and IR absorption image at 1340 cm^{-1} (top right) of a monolayer island film of PEG on gold. An AFM-IR spectrum of one of the PEG islands is shown below

Figure 4 shows the AFM topography image (top left) and an IR absorption image with the IR laser tuned to the fixed wavenumber of 1340 cm^{-1} (top right) of a monolayer island film of PEG on gold. The AFM image indicates the PEG islands are about 4 nm thick. The IR absorption band at 1340 cm^{-1} is assigned to a CH2-wagging mode and the image confirms the location of the PEG island regions. PEG monolayer island regions as small as 25 nm × 25 nm are easily resolved in the IR absorption image. The broad IR band centered at 1102 cm^{-1} is assigned to the C-O-C antisymmetric stretching mod.

Quantifying chemical content in nanoscale polymer domains

Polypropylene (PP) is one of the most important and widely used polymers due to its heat resistance, tensile strength, processability and low cost. However, the applications for PP are often limited by its poor impact resistance, especially at low temperatures. In response, a new copolymerization process had been developed, which allows for the blending of other polymers with PP to improve the overall performance, while increasing high impact resistance.[4]

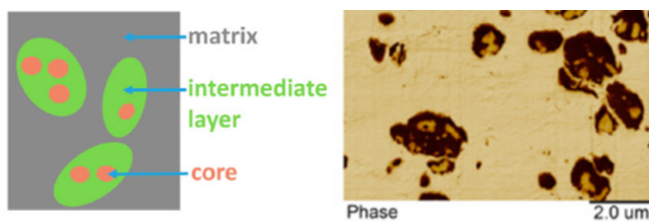


Figure 5: Schematic diagram and AFM phase image showing different regions within high impact polypropylene sample

(HIPP) materials seen in figure 5, show three distinct regions: the matrix, intermediate layer and core. In order to fine tune the performance of HIPP, the ability to probe the chemical composition of each region is necessary.

In general, IR spectroscopy is a powerful tool for the evaluation of chemical composition, however, domains within HIPP are too small to be analyzed by conventional FTIR. On the basis of the strong correlation between conventional FTIR and AFM-IR, FTIR was employed to generate a calibration from standards with known material composition, to correlate the ethylene content in the copolymers with the peak area ratio of the CH2 and CH3 bending bands at ~ 1456 cm^{-1} and ~ 1378 cm^{-1}, respectively.

Figure 6 shows a zoomed in AFM image of the nanoscale domains within HIPP, markers on the image correspond to the location where AFM-IR spectra were collected from the core (red), intermediate layer (blue) and matrix (black).

The collected spectra as seen in figure 7 were normalized to 1378 cm^{-1} to allow for the comparison of the AFM-IR peak ratio data to the FTIR calibration curve as shown in Table 1.

By comparing the peak ratios to the calibration curve created by FTIR, the chemical content of each region can be determined as is shown in Table 2.

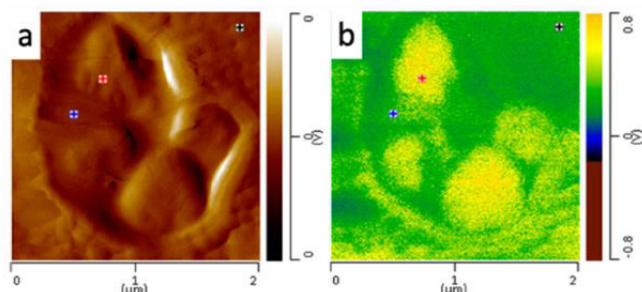


Figure 6: Packaging sample - block face - multilayer sample – seven layers. Reflection mode - hyperspectral imaging - 1 sec/spectra. 1 scan/spectra. 20 x 85 µm size. 1 µm spacing. Image shows carbonyl band and amide II bands and CH bending bands

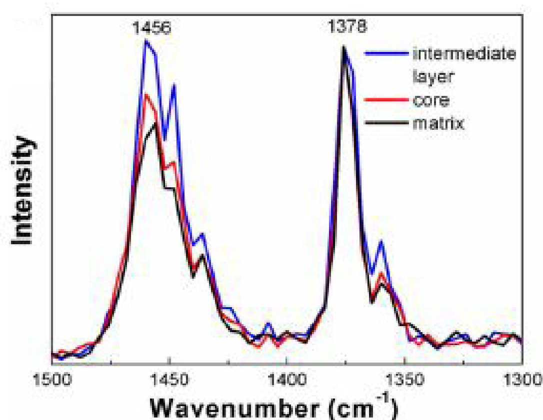


Figure 7: AFM-IR spectra acquired from each region within the HIPP. Data has been normalized to 1378 cm-1

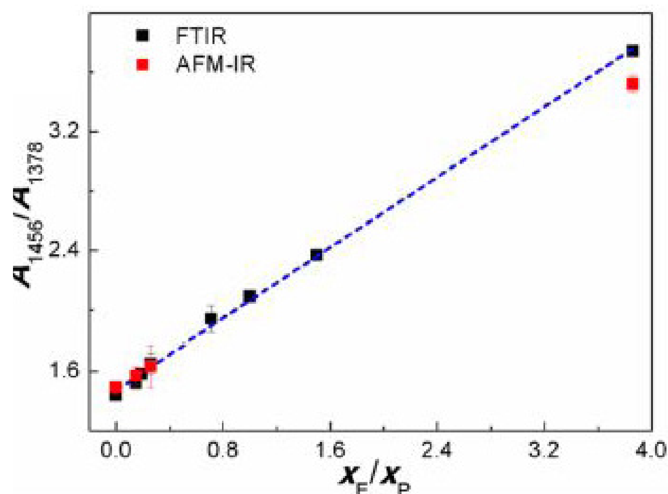


Table 1: Mirage IR spectra collected on the polymer (red) and the defect (blue) region

Domain	Avg. PE Content (wt %)	St. Dev (wt %)
Matrix	2.0	6.0
Intermediate Layer	38.8	10.1
Core	17.2	6.9

Table 2: Average PE content for each domain within HIPP

Conclusions

AFM-IR is a powerful tool for characterizing a variety of polymer materials. By combining the capabilities of AFM and IR spectroscopy, the nanoIR2-FS system can obtain topographical images of the sample surface and characterize the chemical composition of these materials with spatial resolution <20 nm. In this note, we have seen that AFM-IR can be used to characterize or reverse engineer polymer multilayer films, chemically characterize the tie layers between layers in films, and quantify the chemical content of polymer crystallinity with high spatial resolution.

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