

Reverse engineering of polymeric multilayers using AFM-based nanoscale IR spectroscopy and thermal analysis

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Introduction

The identification of unknown multilayer samples is quite similar to solving a Sudoku number puzzle, in which the final solution is deduced from stitching together bits of information in a coherent manner. Often, extraction of such data from ultra-thin layers ($<5\mu\text{m}$) is limited due to either the diffraction limit, in the case of mid-infrared radiation, or the requirement of having a significant amount of material for thermal analysis (TA). Typically, current analytical procedures call for stripping of material by extracting the layers chemically or “peeling” off each layer one-by-one prior to applying the aforementioned analytical techniques. The researcher will then need to reconstruct the information piece-by-piece. Moreover, a great deal of information can potentially be lost or misidentified inadvertently should one of those layers be too thin to be detected.

To keep the structure of the multilayer intact during the analysis, the user could potentially examine the chemistry of the multilayer by taking the cross-section of the film and examining it microscopically, such as by Fourier transform infrared (FT-IR) microspectroscopy or scanning probe microscopy (SPM). Commercially available FT-IR microscopes provide

a nominal spatial resolution of about 3–30 μm in the mid-IR spectral region, depending on wavenumber, but this resolution is insufficient for modern nanoscopic material analysis. SPM can spatially resolve the topography of materials at the nanometer scale. However, despite the abundance of SPM-based surface characterisation techniques, chemical information is not directly available without making assumptions or inferences. With the availability of nanoscale (atomic force microscopy coupled) infrared spectroscopy (AFM-IR) and nanoscale thermal analysis (nanoTA), it is possible to obtain both infrared spectra and transition temperatures of each layer in a cross-sectioned multilayer film. Since both techniques are AFM-based, the topographical features can be readily linked to the spectroscopic and thermal data at a much higher spatial resolution than previously achievable.

AFM-IR and nanoTA techniques

The AFM-IR technique, which was developed by Dazzi *et al.* using the free electron laser (FEL) at Centre Laser Infrarouge d’Orsay (CLIO, Université Paris-Sud, France),¹ takes advantage of the photothermal induced resonance

(PTIR) effect. A laboratory-scale IR light source, tunable between 1200 cm^{-1} and 3600 cm^{-1} , has since been developed for this purpose and been used for recent studies.^{2,3} This AFM-IR technique is based on the rapid thermal expansion of materials that occurs upon absorbing 10ns pulses of IR radiation of a particular wavelength. Directly above that rapid expansion and contraction in space, the AFM cantilever in contact begins to ring from these impulses (Figure 1). Here, the ringdown amplitude of the cantilever is directly related to the absorption coefficient and sample mechanical properties.⁴ Eventually, this ringdown amplitude is used to generate an absorption-like IR spectrum. Even though the sample illumination scheme is similar to attenuated total reflection (ATR), the resulting AFM-IR spectra look more like absorbance spectra derived from transmission measurement FT-IR spectra which, therefore, have good correlation to commercially available mid-IR databases. The nanoTA technique is a well-established technique that offers dramatic sample and time advantages in detecting transition temperatures of materials over conventional thermal analytical techniques, such as differential scanning calorimetry (DSC).

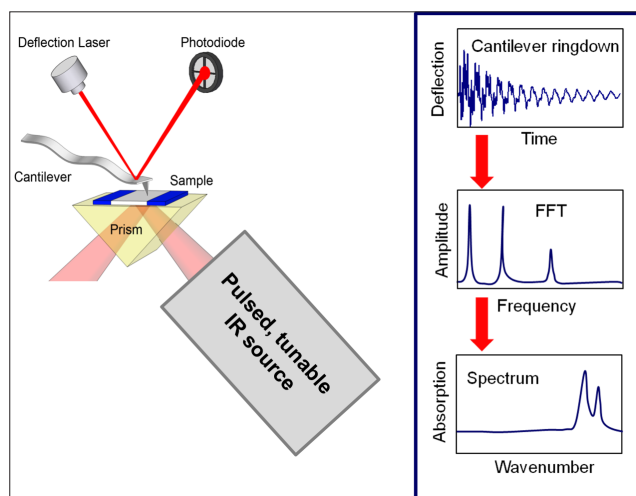


Figure 1. Principle of operation of the AFM-IR technique.

In conventional instrumentation, the sample is heated in its entirety, which may slowly and inadvertently anneal the sample during the course of heating. In essence, this process changes the physical states of the material and the experimental transition temperature may no longer be representative of the sample in its original state. By heating a small local area very rapidly (typical rates of $10^{\circ}\text{C s}^{-1}$ but can achieve above $1000^{\circ}\text{C s}^{-1}$), native transition temperatures can be accurately probed. This high-throughput technique employs a specialised ThermoLever, which has an embedded resistive heating element at the end of the U-shaped cantilever (Figure 2).⁵ Heating occurs when voltage is applied to the cantilever. As the material heats up locally, the material expands and softens to the point where the ThermoLever would penetrate into the sample. These observations are captured by the changes in the deflection of the cantilever during the experiment.

Experimental

The thin multilayer film of unknown composition for this study was embedded in a commercially available two-part epoxy and left to harden overnight prior to being microtomed at ambient temperature. A ~ 700 nm-thick cross-section of the film was transferred from the microtome onto a clean ZnSe prism surface, which it adhered to via weak intermolecular forces. All AFM-IR

measurements were made in a region where the entire film was in good contact with the ZnSe prism. A standard contact mode AFM cantilever, typically either an AppNano SICONA (Santa Clara, CA, USA) or a Mikromasch CSC37-ALBS (Tallin, Estonia), was used to collect the AFM-IR spectra and images. The IR laser power was set to approximately 0.3–0.5 mW by the Analysis Studio software (Anasys Instruments, ver. 3.4). At least three spectra sampled at a data point spacing of 4 cm^{-1} were collected and co-averaged at each location. A one-point smoothing routine was applied to the spectra using the aforementioned software. The IR spectra were calibrated against a polystyrene standard. The spectral resolution of the IR laser was approximately 10 cm^{-1} and the spatial resolution with this sample was expected to be ~ 200 nm. For all nanoTA measurements, a $200\text{ }\mu\text{m}$ Anasys ThermoLever was used to collect thermal transition and topological data. The ThermoLever was calibrated against polycaprolactone, polyethylene and polyethylene terephthalate standards.

AFM-IR analysis of the multilayer film

Structural features and dimensions of the multilayer film can be readily identified by SEM and AFM techniques. The film is composed of six major layers including fillers, which are seen in the SEM and AFM images in Figure 3. At this point,

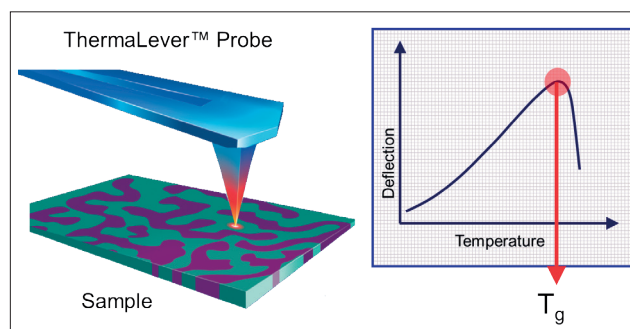


Figure 2. The operating principle of nanoTA.

no specific chemical information can be extracted from these images. This is a typical shortcoming associated with these popular surface techniques.

Using the nanoIR instrument, the infrared signatures of each layer can be identified. After obtaining an AFM image across the film, point-and-click AFM-IR spectra are taken and the composition of each layer is revealed and straightforwardly linked to its topography (Figure 4). At first glance, the spectra of layers 1 and 2 (red and blue traces of Figure 4) appear similar and seem likely to be composed of polyethylene terephthalate (PET). An IR group frequency, consistent with urethane (1516 cm^{-1}), is seen for Layer 3. Layers 4, 5 and 6 share some of the spectral characteristics of polyethylene (1372 cm^{-1} , 1460 cm^{-1} , 2848 cm^{-1} and 2920 cm^{-1}) but absorptions at around

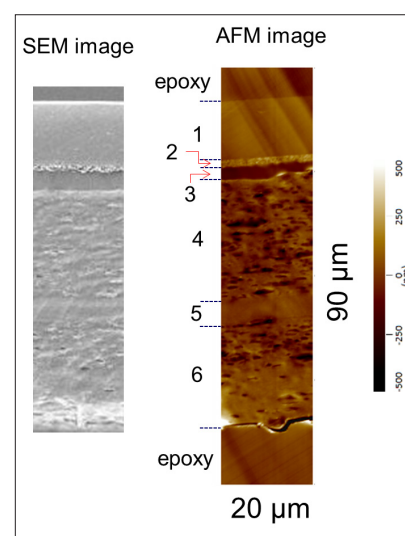


Figure 3. SEM and AFM image of the cross-section of the multilayer film, in which each layer is readily distinguishable.

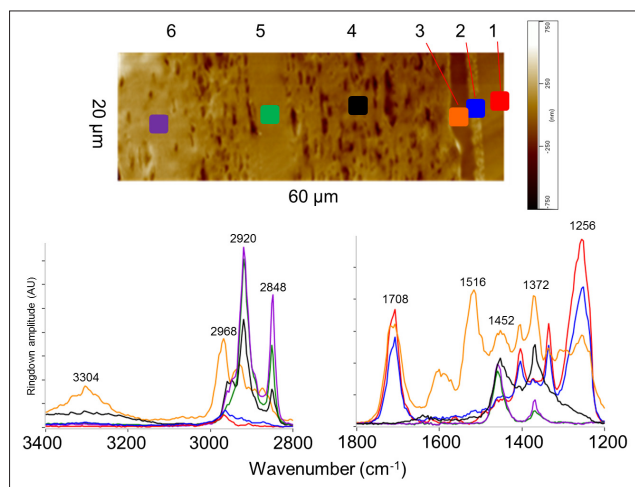


Figure 4. Survey AFM-IR spectra taken at each layer. Top: AFM image of cross-section. Bottom: IR spectra recorded from regions (marked as overlay coloured squares) shown in AFM image; a spectrum colour corresponds to the square colour.

3330 cm^{-1} and 1640 cm^{-1} are also seen for Layer 4 (black trace in Figure 4). Under larger magnification (Figure 5), inclusions in Layer 4 are clearly visible and AFM-IR spectra at several locations are displaying broad absorptions around 3330 cm^{-1} and at 1640 cm^{-1} . In addition, antisymmetric and symmetric CH-stretching bands are strong and sharp; a methyl CH-stretching band is also observed at 2952 cm^{-1} . However, the IR absorption spectrum of the $1.2\text{ }\mu\text{m}$

inclusion lacks these strong bands (blue marker in Figure 6). These data suggest the core component of Layer 4 is polyethylene and the inclusions are hydroxyl-containing materials such as starch or cellulose.

Despite having similarities, Layer 5 is significantly different to Layer 4. In addition to the disappearance of a broad absorption at 3330 cm^{-1} , the shoulder at 2952 cm^{-1} is less apparent. The deformation mode is slightly blue-shifted

(to 1460 cm^{-1}) and the aliphatic antisymmetric CH_2 -stretching absorption band is red-shifted (2916 cm^{-1}). This is possibly due to more ordered polyethylene that has less methyl-terminated ends than that in Layer 4. Layer 5 does not have any inclusions.

AFM-IR spectra suggest that Layer 6 is similar to, yet different from, Layer 4. Topographically and chemically, the inclusions in Layer 6 are similar to ones in Layer 4. The blue spectra in Figure 7 also have broadened absorption features near 3330 cm^{-1} and 1640 cm^{-1} . However, in the middle of the layer there are fewer

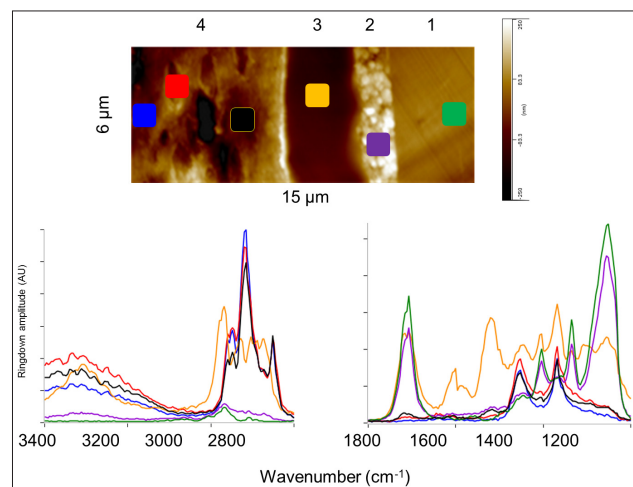


Figure 5. Top: AFM image of layers 1–4. Bottom: IR spectra recorded from regions (marked as overlay coloured squares) shown in AFM image; a spectrum colour corresponds to the square colour.

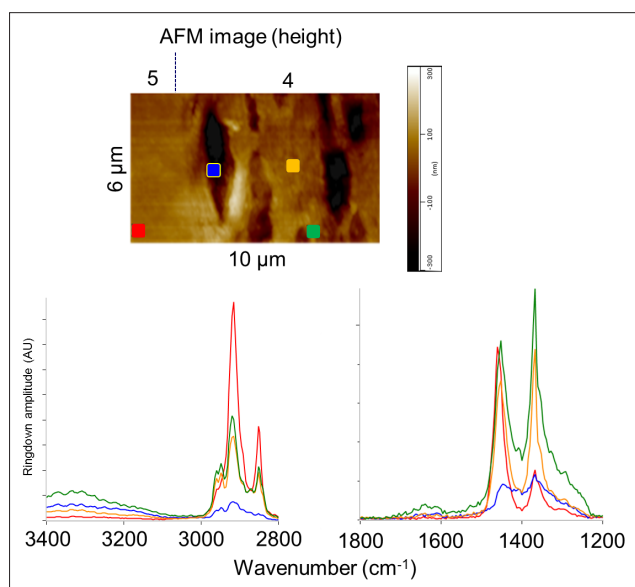


Figure 6. Top: AFM image of layers 4 and 5. Bottom: IR spectra recorded from regions (marked as overlay coloured squares) shown in AFM image; a spectrum colour corresponds to the square colour.

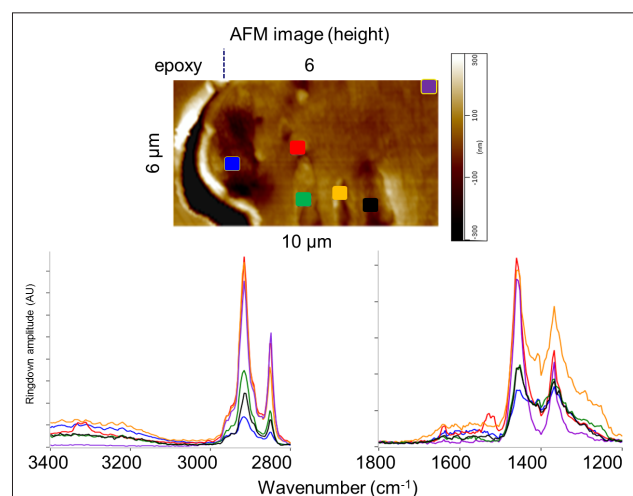


Figure 7. Top: AFM image of layer 6. Bottom: IR spectra recorded from regions (marked as overlay coloured squares) shown in AFM image; a spectrum colour corresponds to the square colour.

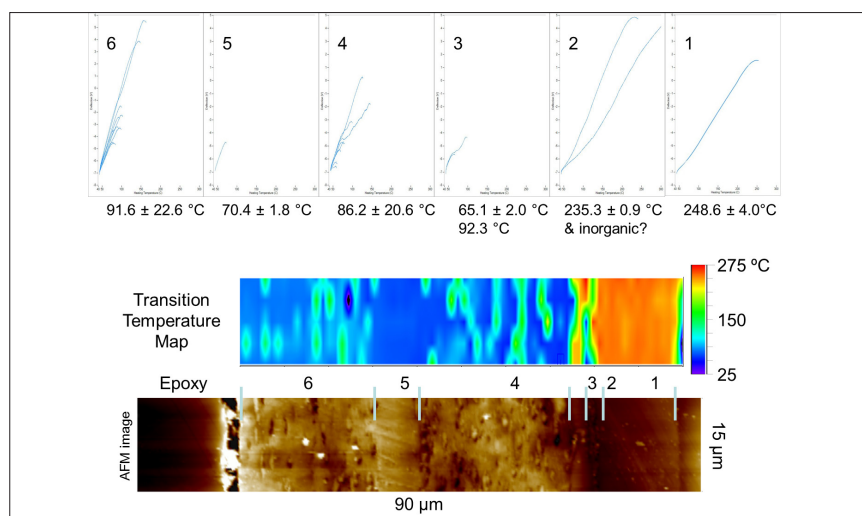


Figure 8. NanoTA thermal traces (top row) and transition temperature map (TTM, middle) corresponding to the AFM image (bottom).

Table 1. Chemical assignment of each layer in a multilayer film based on AFM-IR and nanoTA data.

Layer	Approx. thickness (μm)	Composition
1	14	PET (polyester)
2	1.2	PET+titanium dioxide particulates
3	4.6	PU (polyurethane)
4	20	PE (polyethylene); OH detected in the dispersed indistinct domains
5	5	PE
6	18	Same as layer 4

of those inclusions than the region near Layer 5 (Figure 7). The absorption spectrum associated with the violet marker is consistent with polyethylene. It is also noted the relative band ratio between 1460 cm^{-1} and 1368 cm^{-1} is different in Layer 6 than in Layer 4. This may be due to different molecular weights and/or different amounts of side-branching in the polyethylene.

Nano-TA analysis of the multilayer film

Local thermal analysis of the multilayer sample provides another dimension of analytical data to ascertain its chemical identity. Transition temperature microscopy (TTM) is used to map the spatial variations in softening temperatures across the cross-sectioned multilayer structure. TTM, which maps the softening temperatures across the cross-sectioned multilayer is plotted in

a two-dimensional space, covering every $1\text{ }\mu\text{m}$ in x and $2\text{ }\mu\text{m}$ in y (Figure 8). The 248°C and 235°C softening temperatures in Layers 1 and 2 reaffirm that both layers are composed of PET. Layer 2 may also contain a high melt filler material because no transition can be detected in some of the thermal traces. There is a visible opaqueness with a white tint associated with this layer, suggesting this may be titanium dioxide. Titania in the layer was confirmed separately by electron probe microanalysis (EDS). Two transitions are detected in Layer 3, which corresponds to the hard and soft segments in a polyurethane polymer. The onset melt temperatures as shown by nanoTA for Layers 4 and 6 are near the transition temperature expected for polyethylene but large deviations are detected. This is due to the presence of the hydroxyl-containing inclusions that are scattered within the

layers. By obtaining both localised chemical and localised thermal analysis from a cross-sectioned multilayer film, a profound understanding of its physiochemical properties can be obtained directly.

Summary

Using a combination of nanoscale infrared spectroscopy (AFM-IR) and nanoscale thermal analysis (nanoTA), the composition of a complex multilayer polymer film was deconstructed. (Table 1). Using an AFM cantilever as an IR absorbance detector, the topography of the film's cross-section is directly correlated to the corresponding infrared spectra and transition temperatures at high spatial resolution. Chemical information about the small organic inclusions (as small as $1.2\text{ }\mu\text{m}$) is extracted within Layers 4 and 6. The nanoTA technique determined the transition temperatures of each layer of the cross-section. Not only do the two methods complement and strengthen the validity of the chemical assignments, the chemical and thermal properties can be linked to the spatial and topographic information about the same sample. The results of AFM-IR and nanoTA may be combined with findings from other techniques such as scanning electron microanalysis (SEM) to obtain a full understanding of the material.

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