Identifying contaminants in synthetic polymers and rubbers using micro-ATR FTIR imaging

Application note

Materials Testing and Research

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Introduction

Manufacturing downtime hurts your bottom line — and any downtime caused by unintentional contamination during materials processing is especially painful. With regular adherence to impurity standards and cleanliness specifications it can be significantly reduced.

Contaminants are easily introduced at any stage in the manufacturing process via extraneous input from the factory environment, tooling residue, off-specification raw materials, and minor deviations in processing tolerances. Rapid and effective resolution of any contamination issue relies heavily on ensuring that deviations from critical specifications are rapidly identified and the causes traced.

The low-tolerance, advanced manufacturing of synthetic polymers relies heavily on an ability to understand compositional homogeneity on both the micro and macro-scale. Synthetic rubber polymers can be particularly problematic with regard to operating within fine compositional tolerances because they are commonly compounded with a complex cocktail of different additives. Whether they are plasticizers, vulcanizing agents, protective additives, fillers and materials processing aids — or the unintentional incorporation of contaminants — all additives introduce an additional complexity to the manufacturing process that must be continually and reliably monitored to ensure that the final product meets the desired specification. Since substandard or poorly homogenized synthetic materials can have a huge impact on product integrity, any capacity to reduce defect incorporation, or at least conclusively identify their presence early in the process, will improve manufacturing yield and increase profit margin.

Here we demonstrate how the Agilent Cary 620 FTIR microscope and imaging system can identify defects and monitor compositional variability in a synthetic polymer. Contamination that was introduced during and after production, and heterogeneities in the finished product are all identified. A key advantage of FTIR chemical imaging that sets it apart as an essential tool in polymer quality control is that it can quickly and easily perform qualitative and quantitative analysis of organic and inorganic materials without any sample preparation. FTIR chemical imaging also avoids the surface charging that causes problems for traditional electron and ion beam technologies.

Agilent technologies FTIR imaging microscopes employ a unique "Live ATR imaging with enhanced chemical contrast" feature. Using this, absolutely no sample preparation is needed: samples can be directly examined as received by simply placing them on the motorized microscope sample stage or, if they are particularly elongated (such as the cross-section of a polymer laminate or film), held in a micro-vice sample holder and placed on the sample stage. In all cases, samples can be moved into position under the micro-ATR using the combined visible/IR light microscope objective and analyzed.

Experimental

A large manufacturer of synthetic polymer products contacted Agilent Technologies for assistance in determining the source of a range of small objects that could be frequently observed to contaminate freshly processed samples (Figure 1). The defects clearly had highly variable dimensions and morphologies, and although some appeared intrinsic to the finished product, others appeared more superficial. Accurately characterizing the defects therefore presented a complex analytical challenge.

Analytical approach

Samples were analyzed using an Agilent Cary 620 FTIR imaging microscope coupled to an Agilent Cary 660 FTIR spectrometer. Comprehensive defect analysis of these particular samples proved ideal for a multi-faceted analytical approach and so two types of data were collected:

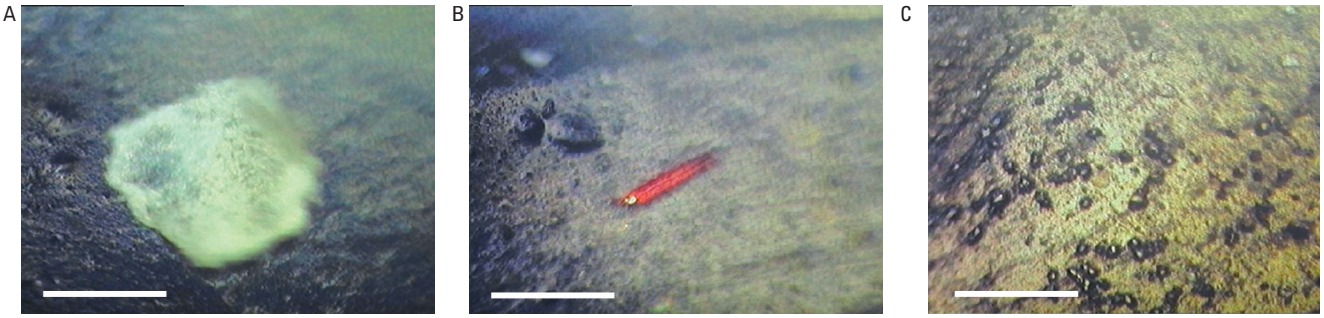

Figure 1. Selected visible light images of the sample. Images were collected using the combined 15x visible/IR objective on a Cary 620 FTIR microscope. Scale bar = 200 µm

- Single point, micro Attenuated Total Reflection (ATR) spectroscopic analyses using the 250 × 250 µm, liquid nitrogen-cooled Mercury Cadmium Telluride (MCT) detector in the microscope
- High-resolution micro-ATR chemical images using a 64 × 64 pixel MCT Focal Plane Array (FPA) microscope detector

Instrument operating parameters are summarized in Table 1.

Sample presentation

During this analysis, no sample preparation was required. Before analysis, the sample was viewed and positioned using the combined visible/IR objective. The unique "Live ATR imaging with enhanced chemical contrast" feature allows for the delicate contact with direct feedback on the quality of contact before data collection.

Defect analysis

The Agilent Cary 620 FTIR microscope and imaging system allowed for a number of different defects to be identified and characterized. The most easily distinguished defects on the polymer surface were roughly spherical, 50–100 µm diameter, white patches (Figure 1A). These could be easily seen with the naked eye and are of obvious concern to a manufacturer focused on providing a high-quality product. Fortunately, their dimensions also rendered them easy to locate under microscope objective and to analyze using single point FTIR micro-spectroscopy.

For every single point micro-FTIR measurement, the analytical area is physically masked by a motorized variable knife-edge aperture blade in the microscope optics. The detector in the microscope then collects all of the light that reaches it from the sample and through the defined aperture blades and an averaged spectrum is displayed. Spatial resolution of single point measurements are typically limited to areas ~20 µm and any chemical heterogeneity within the area defined by the aperture blades is averaged into a resulting overall spectrum, meaning that any subtle spatially distinct chemical heterogeneity may not be detectable. The white spots, however, were larger than this and excellent spectra were collected (Figure 2). Total collection time was <60 seconds, after which the spectrum was automatically matched with those in a spectral library within the Resolutions Pro software package and identified as a polyamide — a compound that was an intrinsic component of the bulk polymer.

Table 1. Agilent Cary 660 FTIR and 620 FTIR microscope configurations

Parameter	Micro-spectroscopic analysis	Chemical imaging
Spectrometer	Cary 660	Cary 660
Microscope	Cary 620	Cary 620
Microscope detector	250 x 250 µm MCT	64 x 64 MCT FPA
Microscope objective	15x Vis/IR	
Microscope accessory	Micro Ge ATR	
Spectral resolution	8 cm^{-1}	
Scans	64	
Spectrum range	4000–900 cm^{-1}	
Total area analyzed	20 x 20 µm	70 x 70 µm
Total number of spectra	1	4096
Measurement Area/Pixel Size	20 x 20 µm	1.1 x 1.1 µm
Total collection time	<60 seconds	

Red, fibrous defects were also relatively common on the sample surface. Single point microanalyses could not be used to characterize them because, as noted above, as the defect was less than 10 µm in diameter and the fact that the detector collects all of the light from the apertured sample area. In this case, the poorer limit of spatial resolution afforded by the technique was insufficient to yield a spectrum that was not dominated by the matrix material (Figure 3).

Chemical images of the sample were collected using an Agilent 64 x 64 FPA detector which is housed alongside the single point detector in the microscope. Switching detectors took place with the click of a button, was entirely software controlled and completed in a couple of seconds. This ensures high-quality, high-spatial resolution data can be quickly generated after the decision to change detector types is made.

Even though the sample presentation technique (micro-ATR) and the analytical collection time (<60 seconds) are nearly identical, data collected by the FPA detector is much more comprehensive than that obtained using single point analysis (Figure 3). Because the FPA comprises a two-dimensional array of micro-detector elements, the detector simultaneously collects 4096 unique full-range spectra from across the entire analytical region of interest with each measurement. Each micro-detector provides a unique spectrum of an approximately ~1x1 µm area of the sample and so the FPA provides, with one snapshot that takes <60 seconds, information that can be immediately displayed by the software as a detailed 2D chemical image of the entire region. The full spectrum recorded by any one of the micro-detectors can be selected for further examination and library searching can be performed by simply clicking at any point on the chemical or visible image.

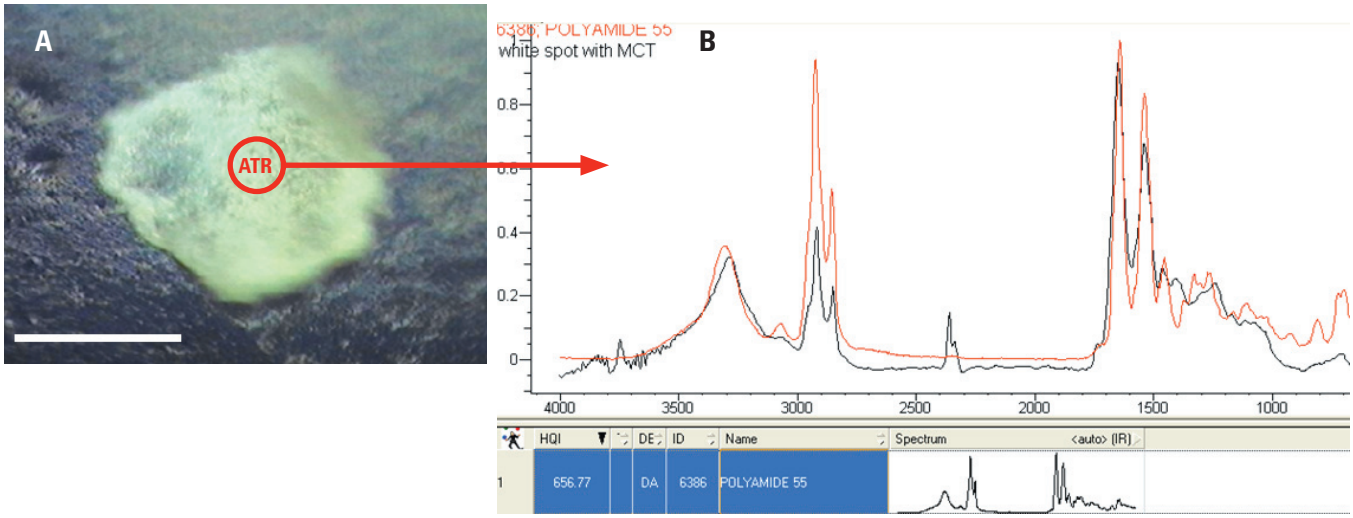

Figure 2. A) Visible image of a white spot on the polymer surface showing the size and location of the analytical region. The image was obtained using the Vis/IR 15x objective on the Cary 620 FTIR microscope. B) Single point ATR spectra collected from the region shown in (A) and the results of spectral library search, indicating the particle is a polyamide (Nylon) Scale bar = 200 µm

Unlike the spectrum collected using the single point detector, which was dominated by the bulk polymer, it was easy to simply click on a "hot" region of the chemical image (one could just as easily interrogate the composition of any region of interest by clicking on the visible image) and extract a spectrum that was characteristic of the defect. By quickly and easily matching it with spectra in a library, the red spot was rapidly identified as a type of cellulose, indicating that it is likely to be a cotton fiber from the local environment.

High-sensitivity, high spatial resolution chemical images that are easily obtained using the Agilent Cary 620 FTIR microscope and imaging system — and with minimal sample preparation — provide an excellent measure of polymer compatibilities and the success of materials processing.

Additionally, chemical images of the bulk polymer showed that it was extremely heterogeneous on the microscale (Figure 4). With a single chemical image collected in <60 seconds with the Ge micro-ATR slide-on accessory coupled to the Agilent Cary 620 FTIR microscope and imaging system, the presence of four distinct chemical components such as polyethylene (PE), nylon, carbonate and the natural rubber matrix, isoprene, were identified (Figure 4). This detailed information is not accessible using any other analytical technique (let alone a non-destructive technique that can enable a novice user to characterize the samples with minimal sample preparation) and was of huge significance to the customer who had ample information with which to reassess the production process.

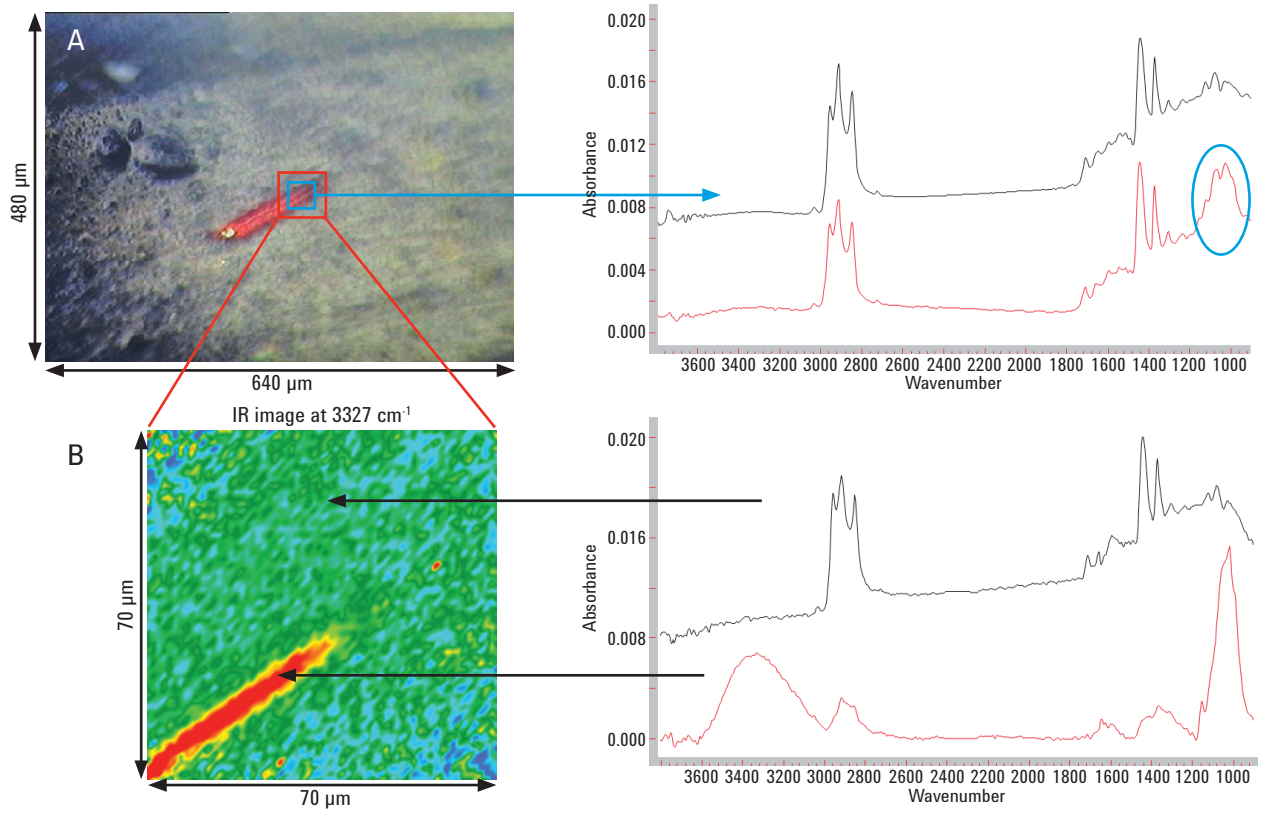

Figure 3. Visible light (A) and chemical images at 3327cm^{-1} (B) of the red fiber defect. Figure 3A also shows the relative dimensions of a single point micro-ATR measurement (blue square) and a micro-ATR chemical image (red square). The single point measurement provided an averaged spectrum for the whole area analysed (40x40 µm) and so does not accurately nor uniquely record the composition of the red fiber. Conversely, although the FPA-micro ATR measurement covers a similar analytical region, Agilent's 64x64 FPA detector simultaneously records and displays 4096 discrete spectra collected at 1.1 µm intervals across the entire analytical region of interest. A spectrum of the defect was then simply extracted from the chemical image (that was collected and displayed in ~60 s. This is the same as a measurement made using the single point detector or a traditional benchtop spectrometer. By clicking on a "hot" region on the image the defect was easily identified as a type of cellulose, most likely a cotton fiber.

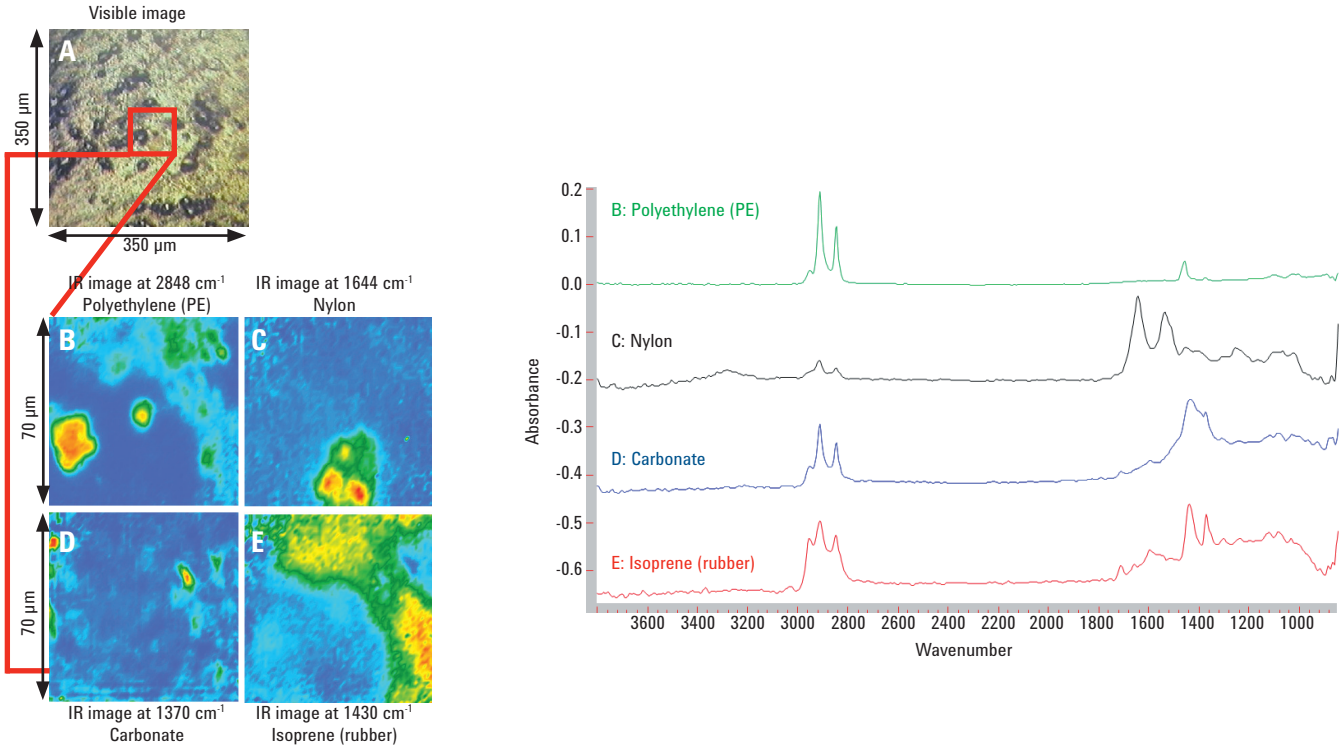

Figure 4. Visible light (A) and chemical images showing the heterogeneous spatial distribution of defects identified from spectral library searches as, B) Polyethylene (PE), C) Nylon, D) Carbonate and E) Isoprene (rubber)

Conclusions

Polymer analysis using the Ge slide-on micro-ATR accessory in single point and chemical imaging (FPA) modes identified numerous discrete defects and compositional domains, quickly and without any sample preparation or sample damage. Micro-ATR chemical imaging is a key analytical method with which to characterize sub 10 µm diameter particles. The non-destructive nature of the technique, coupled with the intrinsic analytical accuracy of the Agilent Cary 620 FTIR microscope and imaging system and Agilent's unique ability to obtain uncompromized characterization data with minimal sample pressure, ensure that with minimal operator training the Agilent Cary 620 FTIR microscope and imaging system is quickly finding a home in production lines to help rapidly:

- Characterize raw materials and assess their purity
- Understand how manufacturing variation influences product stability
- Ensure post-production material homogeneity
- Troubleshoot contamination at any stage of the manufacturing process.

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