Troubleshooting and quality control of polymers using micro-ATR FTIR chemical imaging

Application note

Materials testing and research

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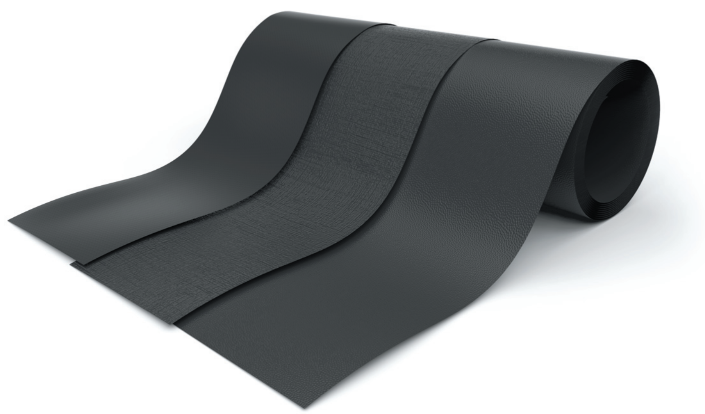

Introduction

In a world where polymer manufacturers face increased pressure to reduce the duration of production cycles and increase product yields, fast and reliable quality control and troubleshooting mechanisms help maximize revenue. A minor hiccup in production can have a significant downstream impact and impose a heavy financial burden. In addition, the incredible speed of modern industrial processes, the diversity and complexity of manufactured products, and the need to provide a complete audit trail for regulatory purposes further heighten already demanding quality control needs. Products that are rejected because they fail to meet specifications can literally cost millions of dollars in lost revenue. Therefore, materials characterization solutions that can accurately monitor product quality and detect and identify contaminants in the shortest possible time frames offer a real opportunity to minimize manufacturing downtime and associated costs, and ensure a valuable competitive edge.

In the production environment, the most valuable materials characterization technologies are non-destructive techniques that allow fast, high sensitivity, and high spatial resolution investigative characterization of samples that can be analyzed as-is by users with minimal experience or training.

Fourier transform Infrared (FTIR) spectroscopy is an established analytical technique that has significant acceptance within the polymer industry. It can uniquely provide detailed information about the structure, composition and purity of polymeric materials, characterize patches of gel, colored specks, fish eyes, holes, wrinkles, scratches and coating voids, help distinguish water drops from oil stains and insects from other contaminants, and help reverse engineer competitor materials.

The Cary 620 FTIR chemical imaging system from Agilent Technologies is a world-leader in spectroscopic innovation and development. It offers the capacity to undertake all of this powerful materials characterization, but with significantly enhanced spatial resolution and with absolutely minimal sample preparation. In this application we use polymer film samples from a production line to demonstrate the effectiveness of the Agilent Cary 620 FTIR microscope as a tool to monitor polymer quality in real-time. We show how easy it is to go from sample to answer in seconds and how this revolution in polymer quality control can help reduce costly delays to production, ensure ultimate product quality and maximize revenue.

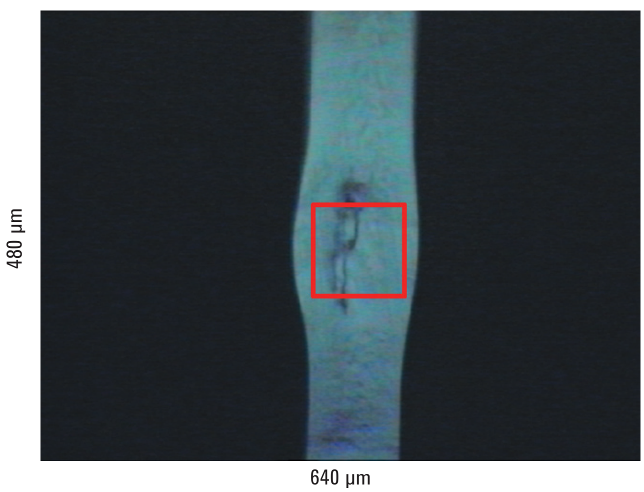

Figure 1. Visible image of the polymer cross-section with the defect of interest clearly visible in the center. The red box shows the location and area of the micro-ATR analysis.

A supplier contacted Agilent Technologies with an example of a key polymer film product. They had conducted preliminary examination with an optical microscope and noted that it was defective (Figure 1), but could not determine the cause. The customer wanted answers quickly to three key questions:

1. What was the defect (i.e., were they compositionally distinct from the bulk polymer?)
2. Why did the defects start to appear in production?
3. When could the manufacturing process safely recommence as soon as possible?

The potential impact of defects on a product can range from simple and cosmetic to so severe that they compromise the overall integrity. A quick and efficient procedure was therefore essential so that the source could be verified and any potential negative impact on production minimized. The supplier had attempted to characterize the defects in their well-equipped materials characterization laboratory but found that traditional methods of defect analysis could either offer molecular characterization but without the required spatial resolution (e.g., FTIR, NMR, GC/MS, LC/MS etc.) or, if they could afford adequate resolution (e.g., different electron and optical microscopic techniques), required destructive sample preparation procedures and/or could offer no useful information about the molecular composition. Without a coupled spatial and compositional solution it was impossible to adequately troubleshoot the problem. The potential that the presence of defects was going to rapidly develop into a critical and costly inconvenience was very concerning for the manufacturer.

Experimental

Sample preparation

The polymer was analyzed as received from the manufacturer. It was simply held vertically in a micro-vice, sectioned with a razor to expose the defect, mounted onto the microscope, and then analyzed (Figure 2). No further sample preparation was required. If the defects are already exposed, the procedure is even simpler: load the sample, focus and then analyze.

This novel experimental procedure, which is unique to Agilent, differs significantly from traditional sample preparation techniques, such as resin embedding, which are normally associated with the compositional analysis of polymer films. Instead of embedding the sample in resin, waiting for it to cure and then carefully grinding and polishing the sample block — a process that can easily take up to 24 hours — with Agilent's unique "Live FPA with enhanced chemical contrast" you can go from sample to answer in minutes.

Instrumentation

The defects and the bulk polymer film sample were characterized using an Agilent Cary 620 FTIR chemical imaging microscope that was coupled to an Agilent Cary 660 FTIR spectrometer. The microscope was equipped with a micro Ge ATR accessory and a 64 × 64 pixel focal plane array (FPA) detector that comprises a two-dimensional array of detector elements (pixels). In this configuration, each pixel of the FPA simultaneously collects a unique infrared spectrum from approximately a 1x1 µm area of the sample. The single measurement took less than 90 seconds to collect. The result was 4096 full energy range (4000–900 cm^{-1}) FTIR spectra, each collected from a unique coordinate on the sample, with a spectral resolution of 8 cm^{-1}. Agilent Resolutions Pro software was then used to automatically display the spectral data as a chemical image. The simplest way to understand this chemical image is to imagine that a pseudo-color (where red is the high and blue is low) is assigned to the height of any characteristic peak on a spectrum (the z-coordinate) and plotted along with the spatial x and y coordinates of each pixel on the detector. The chemical image, therefore, graphically illustrated how compound concentrations vary spatially, i.e., the chemical heterogeneity throughout the sample. Instrument operating parameters are summarized in Tables 1a and 1b.

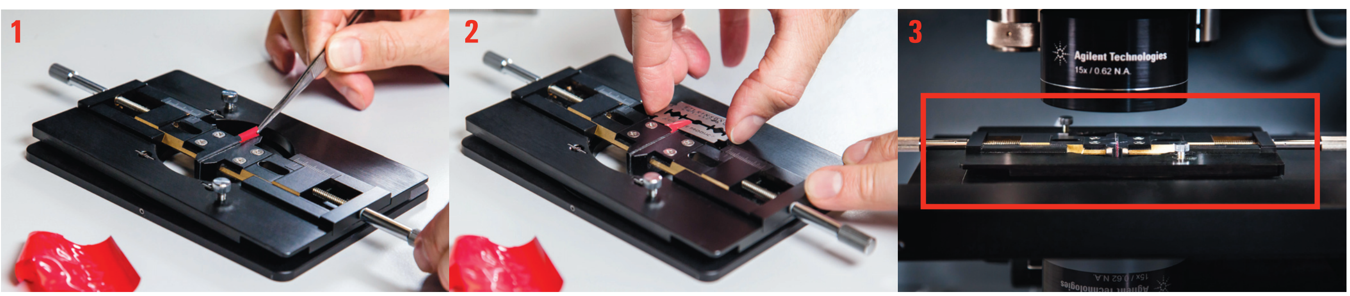

Figure 2. Sample mounting and analytical procedure. 1) Hold the sample in a micro-vice, 2) Cross-section the sample with a razor blade and 3) Place on microscope stage (red box), engage the ATR, and then determine answers in seconds.

Table 1a. Agilent Cary 660 FTIR spectrometer and 620 FTIR microscope configuration

Parameter	Value
Spectrometer	Cary 660
Microscope	Cary 620
Microscope detector	64x64 FPA
Microscope objective	15x Vis/IR
Microscope accessory	Ge Micro ATR
Microscope stage	Micro-Vice
Sample preparation	None
Objective working distance	21 mm

Table 1b. Data collection parameters

Parameter	Value
Spectral resolution	8 cm^{-1}
Scans	64
Spectrum range	4000 – 900 cm^{-1}
Pixel resolution	~1 µm/pixel
Field of View	70x70 µm
Total number of spectra	4096
Total collection time	<90 seconds

Characterization

Measurements were performed using the microscope in micro-ATR mode, and by using Agilent's unique live FPA imaging technique with enhanced chemical contrast. This live FPA imaging technique ensures:

- No resin embedding required. Film samples analyzed 'as-is'
- Excellent data quality by visually illustrating when just the correct amount of sample-ATR pressure is applied
- That the most delicate components are successfully analyzed without damage

The end section of the sample that was held uppermost in the micro-vice was viewed using the 15x visible objective on the Cary 620 FTIR microscope (Figure 1). By then simultaneously observing the sample under the microscope and moving the motorized sample stage, the area of interest was easily and accurately maneuvered under the Ge-micro ATR accessory and the analysis conducted.

Results and discussion

A single analysis, that took about 90 seconds to acquire and which yielded the detailed chemical images shown in Figure 3, was all that was required to accurately characterize the defect in the polymer and assess the likely impact upon the production cycle. Similar data acquired on other FTIR imaging systems would take over a day to analyze, due to time consuming resin embedding and sample preparation.

The chemical image (Figure 3) instantly and quite clearly highlighted a compositionally distinct region within the bulk polymer. The precise nature of this anomalous region was easily and accurately characterized by extracting a spectrum (by clicking on the area of interested within the image) and using Resolutions Pro to automatically compare the spectrum with those contained in a FTIR spectral library, identifying the compound as a type of acryloid. Resolutions Pro software also highlighted that acryloids, the compound that best matched the spectrum of the unknown defect,

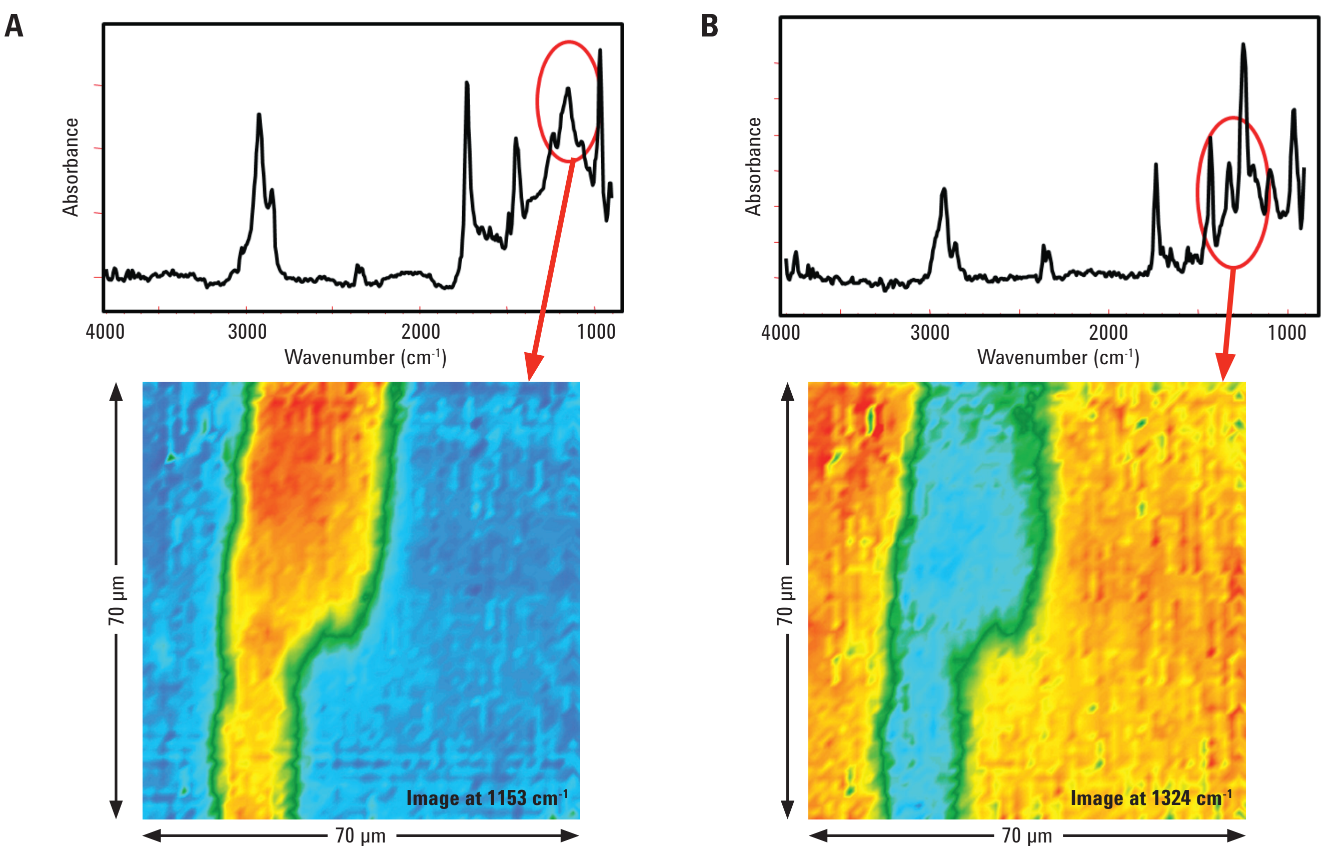

Figure 3. Chemical images and spectra from the measured sample. 3A. A chemical image where warm colors highlight areas of high absorbance intensities associated with what Resolutions Pro identified as an acryloid compound. 3B. A chemical image showing regions where intrinsic absorbances associated with the bulk polymer are present (warm colors) or absent (cool colors).

are commonly used as an impact modifier in polymer formulations, thus further reinforcing the validity of our initial interpretation. Quickly and easily identifying the presence of unmixed impact modifier had serious implications for the manufacturer.

Defects of this morphology have many causes. Some are indicative of serious processing problems and immediately necessitate further detailed investigation because they may lead to extensive and expensive downtime (e.g., extrusion temperature was sub-optimal — which in itself may have many causes), some may indicate a temporary but more easily repairable disruption (e.g., partially worn processing instrumentation) and some are merely a rare or intermittent inconvenience (e.g., a trapped insect).

We have concluded that the defects were caused by extruding a poorly homogenized product. The observed defects occur sporadically and are composed of a compound that we believe was added during production to modify the physical properties of the finished product (we analyzed these samples without any prior knowledge of the material or processing history). Heterogeneities of this character are indicative of poorly melted precursors, and while the reasons for this may be multifold, the ability of the Cary 620 FTIR microscope to provide a robust solution ensured that the minimum amount of time was spent remedying this critical processing problem.

Polymer quality control in the processing plant

The Cary 620 FTIR microscope quickly and easily highlighted regions of unmixed impact modifier within the bulk polymer product. Although the defects were noticed using optical microscopy, their composition — and therefore origin — was unknown. The Agilent Cary 620 FTIR microscope system is still used to perform exactly the same optical examination of the samples but, with the click of a button, can simultaneously also give invaluable compositional information on everything in the microscope field of view. This enhanced analytical capability allows the manufacturer to compositionally examine products in only a few seconds more than the optical examination that was a routine part of the quality control process.

Conclusions

Minimal to no sample preparation, short analysis time and powerful software for automatic data interpretation ensure that the Cary 620 FTIR chemical imaging system is the ideal tool to quickly and reliably troubleshoot polymer products.

Compositional imaging easily identified heterogeneities in the provided sample but the intrinsic power of chemical imaging lies in cases where defects are compositionally, but not optically, distinct from the bulk matrix. Here, even a novice user can progress from sample to answer in seconds — and help reduce costly delays to production, ensure ultimate product quality and maximize revenue that may otherwise pass unnoticed.

Micro-ATR images help identify polymer types, ensure correct materials specification, investigate the composition of copolymers, understand polymer degradation mechanisms, and characterize materials or substances that have not properly homogenized. The range of production issues that can be quickly and easily identified using micro ATR images collected with the Cary 620 FTIR microscope will help improve profitability by increasing yield, reducing costs due to imperfections, and improving overall efficiency.

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