

Characterization of Contaminants in Recycled PET and HDPE using FTIR Microscopy

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Introduction

Reducing environmental pollution and energy consumption in recycling are the paramount driving forces behind research on recycling plastics. The advances in reclamation technologies have pushed the boundaries of recycled plastics or post-consumer resin (PCR) use to include many high-end applications such as food packaging, electronics, and automobiles. These applications often demand near-prime qualities of any recycled plastics. Furthermore, as more and more countries across the globe ban the use of single use plastics, there has been a steady increase in the demand for PCR over virgin resins. To ensure the performance and aesthetic quality of recyclates in second-market applications, it is imperative that fast, reliable, and cost-effective characterization and quality control procedures are implemented at different stages of recycling and manufacturing operations.¹

The challenges in large-scale use of recyclates in the second-market plastic manufacturing arise from the unknown origins of the feedstock, the presence of any contaminants, and possible degradation during previous usage. Traditionally, bulk properties such as melt flow rate and mechanical properties have been used to assess the quality of the recyclates. These macroscopic properties, however, are only indirectly correlated to materials' underlying chemistry and cannot identify contaminants. To that end, FTIR microscopy can provide a more holistic understanding of the material at molecular level by annotating sample morphology with chemical information.

In this application note, we demonstrate the use of FTIR microscopy for the characterization of recycled polyethylene terephthalate (PET) and polyethylene (PE) PCRs. The results show that cellulosic fragments are common contaminants in recycled polymers. Depending on the morphology of the contaminants, different sampling techniques should be adopted for the analysis.

Materials and Methods

FTIR microscopy was carried out using a Thermo Scientific™ Nicolet™ iN10 MX Infrared Imaging Microscope. Three modes of analysis were used: reflection, transmission and micro ATR (μ -ATR). These were applied across different types of sample sets.

For the PET powder sample, an area map was collected in reflectance mode. The PET powders were spread onto a gold slide and analyzed without further sample preparation. The XY area map was collected using an MCT-A detector, 50 μ m spatial resolution, and 8 scans at 8 cm^{-1} spectral resolution at each map point.

For the analysis of the PE pellets, particles were first isolated from the surface of the pellets under a preparatory microscope at 3 \times magnification. Isolated particles were then placed onto a glass slide and analyzed in ATR mode. A slide-on germanium (Ge) tip ATR was used for the analysis of the isolated contaminant particles. An MCT-A detector was used for all samples, and 64 scans at 4 cm^{-1} resolution were collected in 22 seconds for each spectrum. The Ge crystal tip was cleaned between sample analyses using 70% isopropanol.

A grocery bag sample was analyzed as received. A small piece of the grocery bag sample was cut, placed on a transmission holder, and analyzed in transmission mode. An area map with a spatial resolution of 50 μ m was collected, using 4 scans at 8 cm^{-1} spectral resolution at each XY map point.

Results and Discussion

Characterization of Recycled PET Powders by Reflectance FTIR Microscopy

Polyethylene terephthalate (PET) accounts for approximately 10% of the plastic produced worldwide and is extensively used for single use bottle packaging. Figure 1 summarizes the reflectance FTIR microscopy experiments of the recycled PET powders. An area of approximately 2.5 \times 2.5 mm^2 was mapped, in which the PET particles range from tens to hundreds of micrometers in dimension. There are noticeable fibrous features in the optical image (Figure 1A). The FTIR spectrum of the particles (Figure 1C) shows a positive match to PET. The PET spectrum was then used as the reference spectrum for correlation profiling, and the resulting correlation map was superimposed with the optical image (Figure 1B); the warm color indicates a high degree of correlation. Major peaks characteristic to PET, such as 1710 cm^{-1} (the C=O stretching), 1241 cm^{-1} and 1094 cm^{-1} (the C-O stretching), 844 cm^{-1} (trans CH_2 rocking) and 723 cm^{-1} (the aromatic C-H out-of-plane bending), are observed in both the sample spectrum (red) and reference spectrum (blue). Note that the peak at 3430 cm^{-1} , attributed to the hydroxyl groups, shows a higher relative intensity in the recycled PET. The chain scissions during PET recycling could generate polymer radicals with hydroxyl groups.²

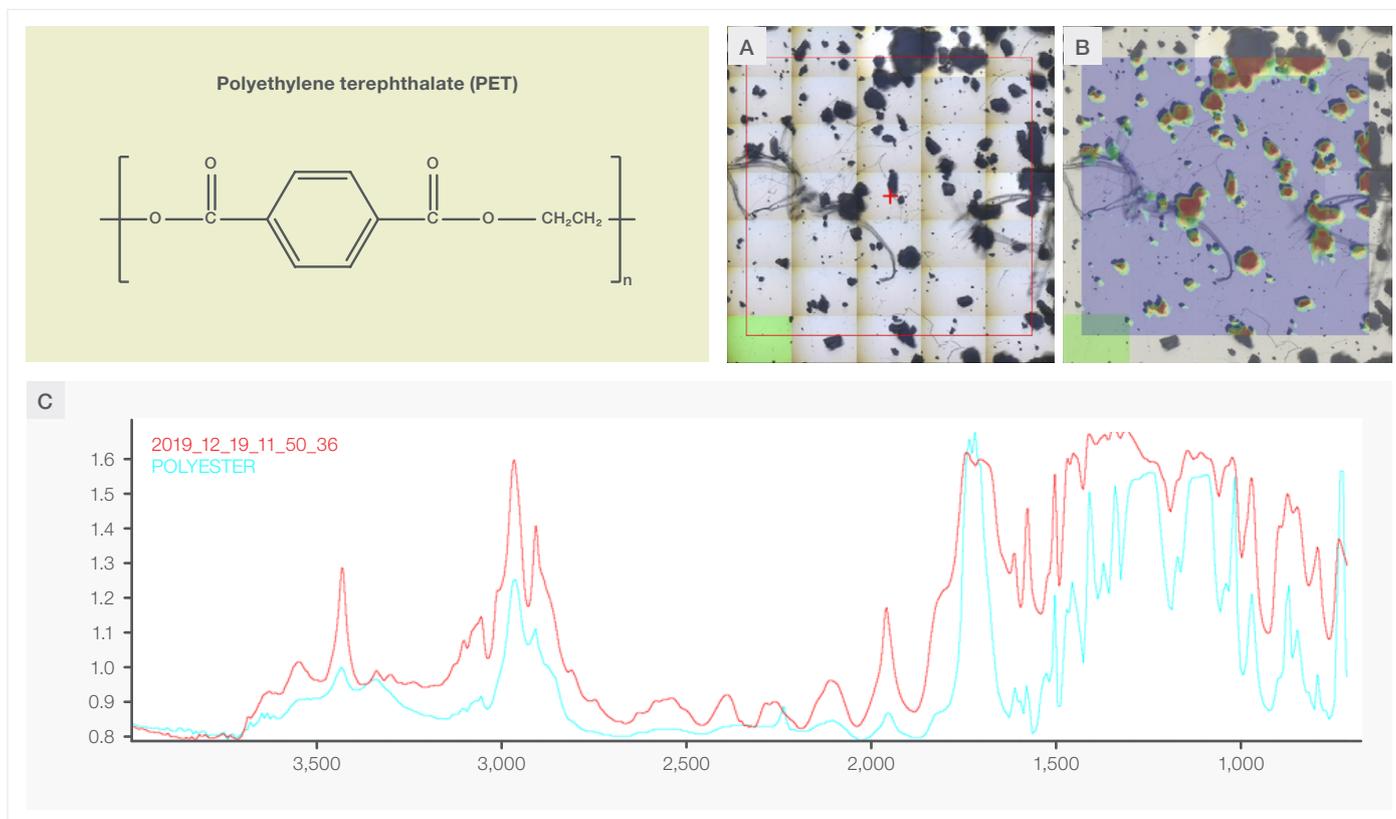


Figure 1. Analysis of recycled PET powders using reflectance FTIR microscopy. (A) Optical image of the recycled PET powders spread on a gold slide. (B) Chemical image superimposed with the optical image. The chemical image is the correlation profile using the PET spectrum as the reference. (C) Reflectance FTIR spectra of the recycled PET particles (red) and the standard reference spectrum from the library (blue).

The same procedure was repeated for the fibrous features observed in the optical image (Figure 2A). The resulting spectrum (Figure 2C) shows a positive match to cellulose. The observed peaks in the spectral range of 3600 - 2900 cm^{-1} are characteristic for the stretching vibrations of the O-H and C-H bonds in polysaccharides: the band at $\sim 2900 \text{ cm}^{-1}$ is attributed to the C-H stretching vibration of the hydrocarbon constituent, and the broad peak centered at 3300 cm^{-1} is ascribed to the stretching vibration of the hydroxyl group, including both inter- and intra-molecular hydrogen bond vibrations. In the fingerprint region, the peaks located at $\sim 1640 \text{ cm}^{-1}$ correspond to the vibration of water molecules absorbed in cellulose. The absorption bands at 1428, 1367, 1334, 1027 and 896 cm^{-1} arise from stretching and bending vibrations of $-\text{CH}_2$ and $-\text{CH}$, $-\text{OH}$ and C-O bonds in cellulose.³ Cellulose is mainly used to produce paperboard and paper and therefore it is a common contaminant found in recycled polymers, possibly originating from labels and stickers on many consumer products. Cellulosic contaminants are undesirable as they can be cascaded into the end products, negatively affecting the products' performance and aesthetic.

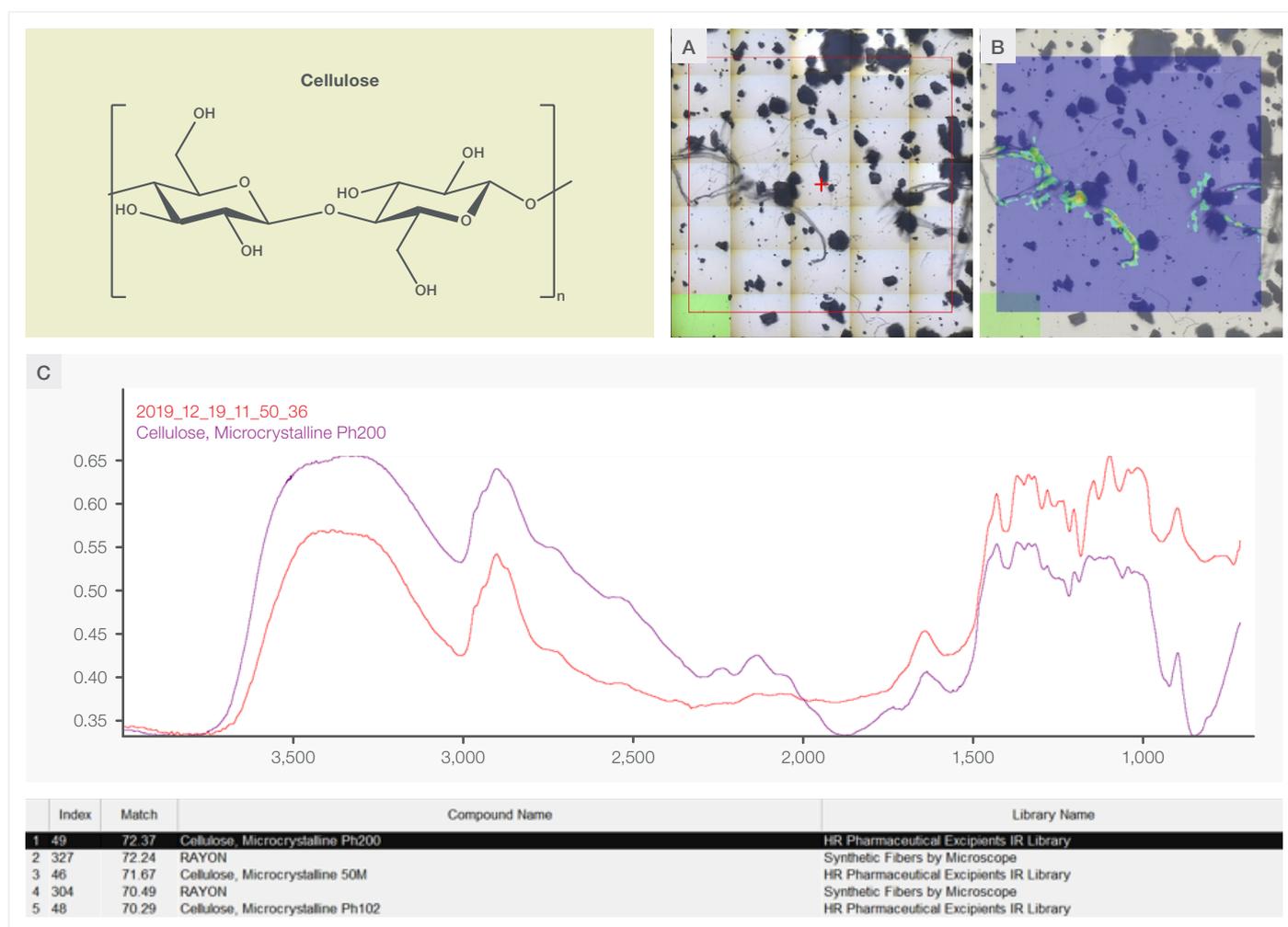


Figure 2. Analysis of the fibers in the recycled PET powders using reflectance FTIR microscopy. (A) Optical image of the recycled PET powders spread on a gold slide. (B) Chemical image superimposed with the optical image. The chemical image is the correlation profile using the cellulose spectrum as the reference. (C) Reflectance FTIR spectrum of the cellulose fibers (red) and the standard reference spectrum from the library (purple).

Analysis of the Contaminants in Recycled HDPE Pellets by ATR FTIR Microscopy

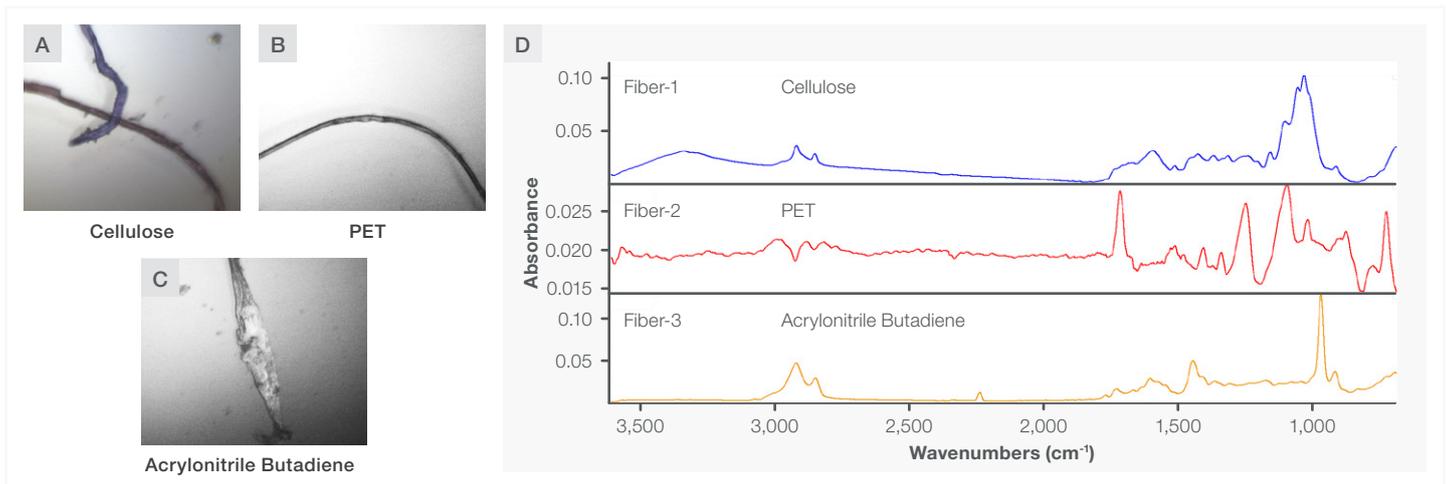


Figure 3. μ -ATR FTIR microscopy of recycled PE pellets.

The FTIR microscopic analysis shows that there are at least three types of fibers present in the recycled HDPE pellets: cellulose (Figure 3A), PET (Figure 3B) and acrylonitrile butadiene (Figure 3C). The representative FTIR spectra of the three types of fibers are shown in Figure 3D, where the fibers can be readily differentiated.

In the same pellet sample, there are visually discernible black particles (insert of Figure 4). The particles were isolated from the pellet and subjected to μ -ATR FTIR microscopy analysis. The results are shown in Figure 4. Upon library search, the particles show a match to cellulose but with a low matching value. Most likely, these particles are charred cellulose. There are pronounced differences in FTIR spectra across the whole spectral range between cellulose and the particles. In particular, the peaks associated with the O-H group, such as those at 3600-3100 cm⁻¹ (stretching vibration of the hydrogen bonded O-H in polysaccharides), 1630-1650 cm⁻¹ (the O-H bending from the water molecules absorbed in cellulose), and 2940 and 2860 cm⁻¹ (asymmetric and symmetric stretching vibrations of the C-H hydroxyl groups), are either absent or present at much lower intensities, suggesting the dehydration reactions during the cellulose \rightarrow charred cellulose transformation. In addition, the peak at \sim 900 cm⁻¹, which is attributed to β -glycosidic linkage between glucose units, is absent, suggesting the breakage of the pyranose linkage in cellulose. The peaks associated with the pyranose, such as those at 1428 cm⁻¹ and 1370 cm⁻¹ (CH₂ and CH bending of pyranose ring), and 1034 cm⁻¹ (C-O-C pyranose ring vibration), are preserved but with decreased intensity⁴⁻⁵.

It should be noted that μ -ATR often provides the best S/N for the resulting spectrum, which lends itself to library searching. In addition, it requires little to no sample preparation, whereas other modes of analysis often involve sample preparation steps such as flattening the samples for reflectance analysis or compressing the samples into thin sections for transmission analysis.

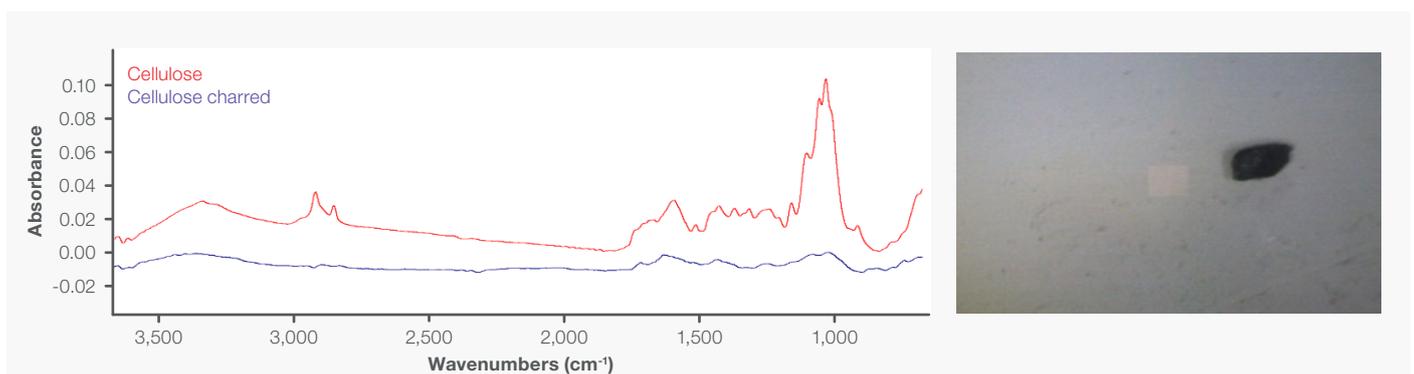


Figure 4. ATR FTIR spectrum of a black particle in the recycled PE pellets.

Analysis of the Particles Present in Grocery Bags by Transmission FTIR Microscopy

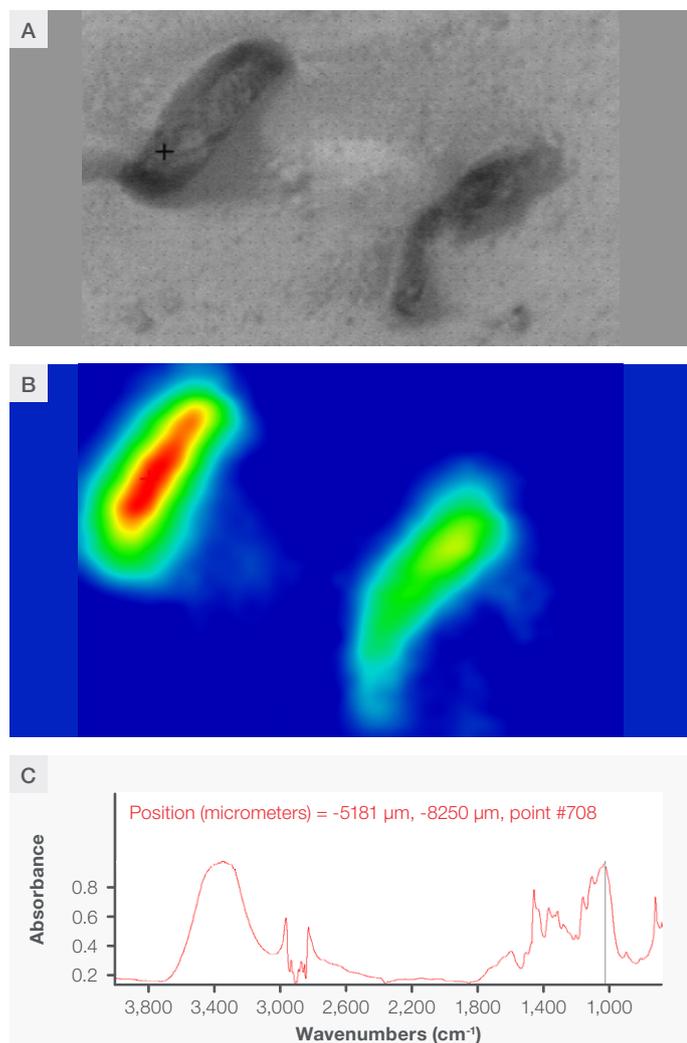


Figure 5. Transmission FTIR microscopy of grocery bag made from recycled LDPE. (A) Optical image of a piece of grocery bag showing two particles embedded in the sample matrix. (B) Chemical map of the sample constructed using cellulose spectrum as the reference. (C) FTIR spectrum of the grocery bag sample with PE spectrum subtracted.

The grocery bag was made out of recycled LDPE. A small piece was cut and analyzed in the transmission mode with no further sample preparation. Two particles were located (Figure 5A). Due to the thickness of the film, the peaks are saturated. In order to extract the spectrum of the contaminant particles, the PE peaks were subtracted from the total spectrum and the resulting spectrum is shown in Figure 5C. The ensuing search shows a match to cellulose. Correlation profiling using the cellulose spectrum results in the chemical image shown in Figure 5B.

Conclusions

In this application note, FTIR microscopy was successfully applied for the analyses of the contaminants found in recycled polymers. In all samples analyzed, cellulose, in either its native or charred form, was identified as a contaminant. The comparison between cellulose and charred cellulose provides an insight to the difference in their underlying chemistry, which can be beneficial for understanding the origins of the contaminants as well as their associated recycling processes. Additional fibrous contaminants, PET, and acrylonitrile butadiene, were identified in the recycled HDPE pellets, illustrating the chemical specificity of FTIR microscopy. Three sampling modes—reflectance, μ -ATR, and transmission—were used for the analyses, demonstrating the flexibility and versatility of FTIR microscopy to suite different sample types.

References

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