PROCESS MONITORING FOR RECYCLED POLYMER EXTRUSION

Raman spectroscopy is a highly-selective and nondestructive optical spectroscopy technique which relies on the inelastic scattering of laser light to probe molecular structure. The non-destructive nature of Raman measurements along with the molecular specificity of the spectra make it an optimal technique to monitor manufacturing processes in real time. The use of Raman can facilitate process understanding and allow effective process control, thus helping minimize production errors.

Background

Polymer extrusion is a high volume manufacturing process which converts raw plastic pellets into a uniform material. For certain processes, recycled raw materials are used. Working with raw materials from secondary sources poses unique difficulties with respect to keeping a process under control. Materials will inevitably come from a wide variety of origins and must be pre-treated to ensure the material is as 'clean' as possible. Intuitively, however, in such situations one would expect that confirming batch-to-batch consistency, certifying suppliers, and checking the suitability of each batch will be challenging.

For the process of interest in this case, each incoming batch of recycled raw material is inspected using traditional measurements such as tests for viscosity, which are, in turn, used to infer the molecular weight and predict melt properties. The batch is duly certified based on this measurement and placed in the queue for use in production. Further attempts are made to exclude unsuitable materials with QC testing that involves monitoring pressure and temperature using a pilot extruder.

This approach makes the process, at best, highly susceptible to variability in final product quality and, at worst, at risk with regard to using unsuitable material which can jam the extruder or break threading leading to a full stop on the manufacturing line. It is clear that a better means of both material confirmation and process control would alleviate risk.

Raman spectroscopy has been definitively shown to be suitable for characterizing Polyethylene Terephthalate (PET) solid, the polymer of interest in this case. PET is used in plastic water bottles and as an additive woven into polyester yarn for clothing. By using Raman spectroscopy for in-line measurements of the polymer melt, the material properties can be determined in real time; suppliers can be characterized and possible degradants and impurities can be detected allowing the process engineer to react quicker to ever-changing production conditions. This capability conveys the potential for better process understanding and control.

Experimental Conditions

Working with the Repreve® Recycling Center (RRC) of Unifi Inc. at the Mebane Complex in Yadkinville, NC, a HyperFlux P.R.O. was installed in the laboratory where all incoming raw and process materials are checked. A Raman spectrometer configured with a 785-nm laser source and a fiber optic probe was interfaced with a Dr. Collin Miniextruder. The probe was fabricated for a standard Dynisco-type connector. This fitting makes allowance for installation into any extruder with temperature and pressure probe ports (see Figure 1).

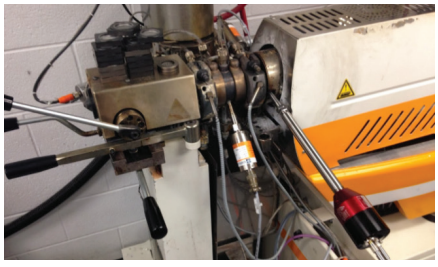

Figure 1 - Dynisco compatible probe conducting Raman measurements of polymer melt

The HyperFlux PRO used in this study had a bandpass of approximately 230 – 3200 cm^{-1} with a 4.4 cm^{-1} average resolution. This allowed for collection of data ranging from the fingerprint region to the longer C-H stretches. The High-Throughput Virtual Slit (HTVS) technology allowed spectra to be captured every 2 s with good SNR using an excitation laser power of 450 mW.

Results

The ability to properly characterize and qualify different suppliers was initially demonstrated. Figure 2 shows the raw melt spectrum of the Virgin (non-recycled) PET melt. The peaks observed match well to the literature references on relevant PET bands used for characterizing properties such as density and molecular weight. For example, the ratio of the bands at 1730 cm^{-1} and 700 cm^{-1} is well correlated to density. Other regions give information with respect to molecular weight, orientation, and a variety of other polymer properties.

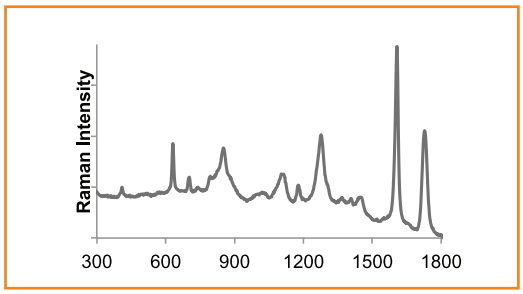

Figure 2 - Raman spectrum of Virgin PET melt

Fifteen-minute extruder trials were conducted on a series of different polymers, which included Virgin PET, processed recycled PET, and supplier-provided raw PET. The resulting spectra were then processed and analyzed using Principal Components Analysis (PCA) with only a derivative for preprocessing. The PCA was, with high accuracy, able to differentiate the different polymer types (as expected), and to differentiate the various suppliers of the raw unprocessed PET. This suggested there were chemical differences among supplier materials (Figure 3). Once the material was processed and re-run through the extruder, the accuracy of the prediction decreased but remained acceptable. This result was expected and indicated that the recycling operation was producing material similar to the Virgin PET.

Finally, several days of data, resulting in thousands of spectra, were analyzed to compare the Virgin PET from recycled PET and a recycled PET blend. By processing the data using a Standard Normal Variate (SNV) correction, the spectra were well correlated even over multiple days, indicating the calibration was robust over time, as suggested in Figure 4.

To ensure that the differences being detected were chemical in nature, the group difference between the Virgin material and recycled material was investigated, as shown in Figure 5. In addition to the expected differences in peak ratios in comparison to the raw Virgin spectra, a peak at 1000 cm^{-1} appears 'negative' in the group contribution plot indicating this is non-existent in the Virgin spectra; Raman peaks at 1000 cm^{-1} are indicative of an aromatic ring mode.

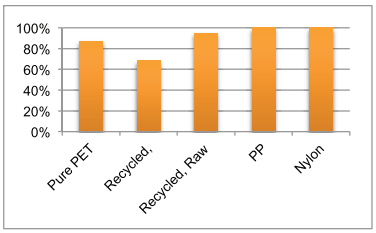

Figure 3 - Single day trials showed excellent discrimination abilities between highly similar materials

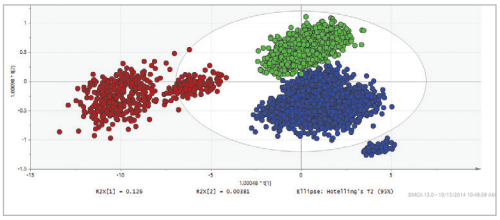

Figure 4 - PCA factor plot showing excellent separation of thousands of spectra over multiple days

It is currently believed that this may be diagnostic of poorer quality recycled material in which ortho- or meta-linkages in the PET chain are created. Such a phenomenon would manifest the observed aromatic peak.

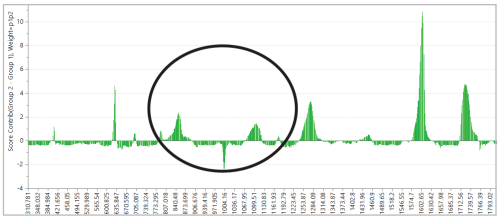

Figure 5 - Group contribution plot of Virgin-recycled polymer

Conclusion

The HyperFlux PRO enabled new insights into a recycled polymer extrusion process, which allows for improved product quality, better process efficiency, and a deeper understanding of the incoming materials to enable superior process control.

Tornado Spectral Systems
705-555 Richmond St. W.
Toronto, ON
www.tornado-spectral.com

Phone: +1 416.361.3444
Fax: +1 416.361.6374
sales@tornado-spectral.com

Tornado Spectral Systems
2359 N. Triphammer Rd.
Ithaca, New York

Phone: +1 607.379.6185
Fax: +1 607.697.0408
sales@tornado-spectral.com