In-line monitoring of ethylene vinyl acetate copolymer with Raman spectroscopy

Benefits at a glance
- Non-invasive in-line analysis of history-dependent materials
- Real-time acquisition of molecular-level information
- Remote sampling using fiber optics

Introduction

Ethylene vinyl acetate (EVA) copolymer is a versatile material used in a variety of applications, depending upon the ratio of the two monomers. In order to ensure consistent quality of this polymeric product, a method of monitoring the polymer melt as it is produced is needed. Traditional on-line and at-line methods involve manipulation of the sample that can lead to changes in the sample, causing it to become unrepresentative of the batch at large. Because the measured properties of a polymer melt depend on the history of the sample with regard to stress, strain, strain rate, and temperature, the ideal method of analyzing a polymer melt would involve non-invasive in-line sampling in real time.

Several techniques including rheometric, optical, ultrasonic, and electrical methods have been used successfully to gain information about bulk physical properties of a polymer melt. In this work, modern spectroscopic techniques that can give information on the molecular level and are amenable to in-line analysis were evaluated for this application.[1]

Experimental

Samples of EVA copolymer (Figure 1) of varying composition between 2 and 43.1 wt% vinyl acetate (VA) were extruded using a single-screw extruder at a set melt temperature of 180℃ and a constant screw speed of 15 rpm.

A Raman analyzer equipped with a 785 nm laser and a CCD detector was used to collect Raman spectra. The Raman analyzer was interfaced to the extruder barrel using a proprietary high-pressure in-line optic. Spectra were acquired every minute using a single 28 second acquisition. The fluorescence background was removed by calculating the first derivative of the spectra. The first-derivative spectra were then mean centered and subjected to a one-factor partial least squares (PLS) regression analysis.
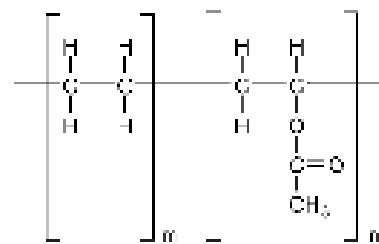

Figure 1: Ethylene vinyl acetate (EVA) copolymer

The samples were also analyzed using near-infrared (NIR) spectroscopy.

Results and discussion

Raman spectra of EVA copolymer melts with 2% (a) and 34.2% (b) VA are shown in Figure 2. Characteristic VA bands are found at 630 (O–C=O deformation) and 1740 cm^{-1} (C=O stretch).
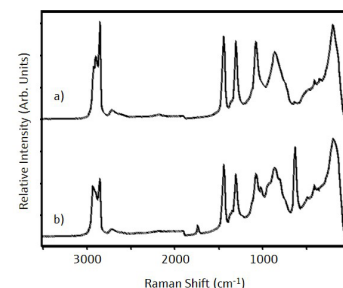

Figure 2: In-line Raman spectra of EVA copolymer melts showing characteristic VA bands

ⓘ All Raman analyzers and probes referenced in this application note are Endress+Hauser products powered by Kaiser Raman technology.

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The sequential extrusion of each copolymer, from lower to greater VA content, was monitored in real time by Raman spectroscopy. The area of the O−C=O deformation band at 630 cm^{-1} increased in a stepwise fashion as polymer with greater and greater VA content was extruded (Figure 3).
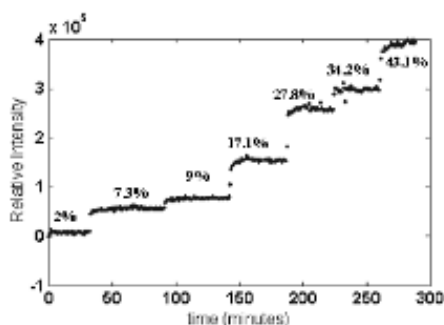

Figure 3: Stepwise increase in 630 cm^{-1} band intensity as EVA copolymers with increasing VA content are extruded

Figure 4 compares the VA content determined by thermogravimetric analysis (TGA) compared to the prediction from the one-factor PLS model. The standard error of prediction (SEP) was 0.56%.
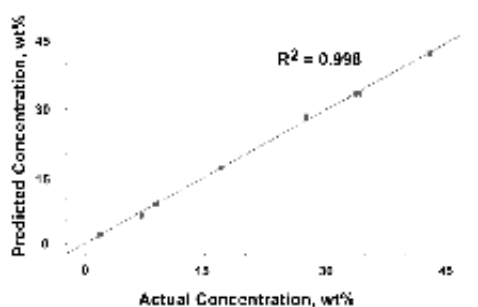

Figure 4: One-factor PLS results for Raman data versus actual concentration

Conclusion

These results show that Raman spectroscopy is a viable, robust method for in-line monitoring of the production of copolymers. Raman spectroscopy is particularly suited to in-line analysis because it is a scattering technique, so only a single optical probe is needed, rather than an invasive dual transmission probe. In this work, the Raman probe tip was aligned so that it was flush with the interior of the process apparatus, rather than intruding into it and causing a disruption of the process flow.

The visible and near-infrared excitation radiation used in Raman spectroscopy makes it suitable for use with fiber optics, which allowed the Raman probe to be incorporated into the extruder with the analyzer (laser, spectrometer, electronics) located remotely.

Other spectroscopic techniques are less suited for in-line analysis of history-dependent materials. Mid-infrared spectroscopy (MIR) requires short path lengths and therefore the sample is often removed from the process by a side stream and analyzed in a temperature and pressure-controlled cell. NIR gives less qualitative chemical information than either MIR or Raman spectroscopy due to the nature of its overtones and combination bands. Such features are difficult to relate to specific chemical species, limiting the analyst's ability to gain understanding during process development. NIR typically requires transmission probes, which in this application interfered with the melt flow and created problems with the rheology and shear heating of the polymer. The volume of an in-line transmission probe can cause changes in the process mixing, induce turbulent flow, or act as a fouling mechanism. The NIR probes used here are not standard fittings, so they could not be easily implemented into a range of processes.

Raman spectroscopy was the only technique evaluated that combined the advantages of high information content and high sensitivity with simple, versatile, non-invasive sampling.

References

1. Barnes, S.E.; Sibley, M.G.; Brown, E.C.; Edwards, H.G.M.; Scowen, I.J.; Coates, P.D.; Baker, W. "Real-Time Monitoring of Ethylene Vinyl Acetate Extrusion using Process Spectroscopy" *Proceedings of Polymer Process Engineering–PPE 03: Enhanced Polymer Processing*, University of Bradford, Bradford, 2003: **342–358**.

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