Applications of process spectroscopy to polymer melt processing

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Process Column edited by John Andrews and Paul Dallin

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Preamble

The polymer industry has proved a fertile ground for the growth of spectroscopic measurements. High product volumes coupled with customised user products and stringent quality parameters, have required the development of rapid and accurate analytical techniques. Many of these methods have been spectroscopic, but mainly off-line [casting a thin polymer film for transmission Fourier transform infrared (FT-IR)] or near line [polymer pellet composition by reflectance near infrared (NIR)]. However, the real payback is obtained by entering the high temperature, high pressure, high volume world of the polymer melt.—*John Andrews and Paul Dallin*

Introduction

Over the last decade there has been an increased drive in the polymer industry for the use of on-line and in-line monitoring techniques for analysis and control of polymer production processes. The significant interest in these fields is due to increasing economic, legislative and ecological demands for consistent quality of polymeric raw materials and products.[1]

Polymer extrusion forms the basic process for manufacture of a huge range of plastic products ranging from micro-scale implants for biomedical applications to major vehicle components. Hence control of the extrusion process is of paramount importance to a massive number of industries. A simple polymer extruder accepts polymer pellets at a cooled feed zone of a rotating Archimedean screw. This conveys the polymer through a temperature-controlled extruder barrel where the material is melted by both frictional heat and heat conducted from the barrel heaters. Polymer is compressed and homogenised along the barrel before emergence through an exit die of a required geometry to form the product.[2] Polymer processing relies upon high temperatures (greater than 200°C) in order to melt the base resin and typical industrial pressures (for extrusion and injection moulding) of several hundred bar.

An efficient process control system should ideally rely on in-process analysis of polymer characteristics during manufacturing providing real-time assessment of polymer properties such as structure, morphology and composition.[3] The use of in-process spectroscopy allows molecular-specific information to be extracted from the melt flow as opposed to physical information (such as temperature, pressure and rheological measurements) derived from more conventional in-line methods. These more conventional process control techniques do not provide information on all variations in material properties especially when analysing complex polymer systems and reactive extrusion processes.[4]

Process monitoring techniques applied in a industrial environment must be robust enough to withstand hostile processing conditions such as elevated temperatures, high pressures, fluctuating conditions and electrical noise.[3] Recent advances in fibre optic technology and the development of robust high temperature and pressure tolerating probes has allowed a range of real-time spectroscopic measurements to be taken from the melt in a non-invasive manner. On-line analysis is also available where the sample is drawn from the process line by the use of a gear pump and transported to a measurement cell. Each approach has its advantage and disadvantages.[3,5] On-line techniques involve sampling delays (in the order of several minutes) and may add strain and temperature history to the material whereas in-line techniques conduct measurements directly in the melt stream and delays are therefore short or non-existent.[5] However, in-line techniques may interfere with the main process and can be affected by fluctuations in melt temperature and pressure, whereas on-line measurements are conducted away from the main process in a cell where temperature and pressure are better controlled.[3,4]

Applications

At Bradford University, we have implemented on-line transmission mid-infrared (MIR), on-line near-infrared (NIR), in-line transmission NIR and in-line Raman spectroscopy alongside other analytical techniques such as ultrasound transit time measurements to monitor composition of polymer blends and copolymers during extrusion.

Real-time analyses of polyethylene/polypropylene blend composition[4,6] and determination of the vinyl acetate content of a series of poly (ethylene vinyl acetate) copolymers[7] have been conducted during single screw extrusion at typical temperatures of 200°C, screw speeds of 15 rpm and pressures up to 35 bar.

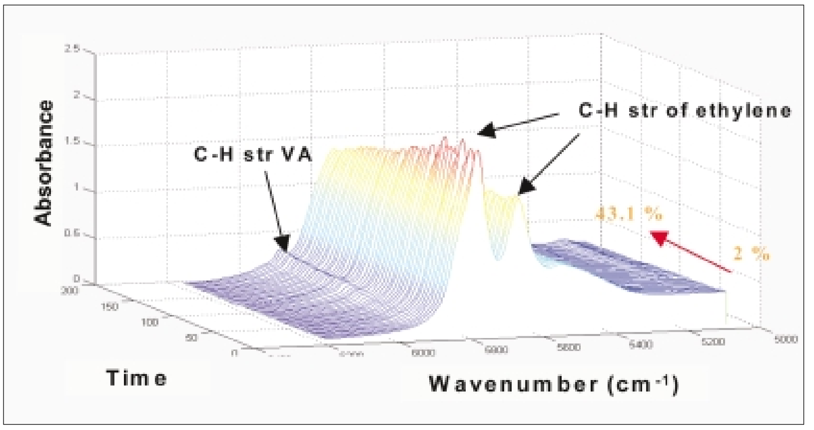

Figure 1. NIR spectra of a series of PEVA copolymers with varying VA content acquired in-line during extrusion.

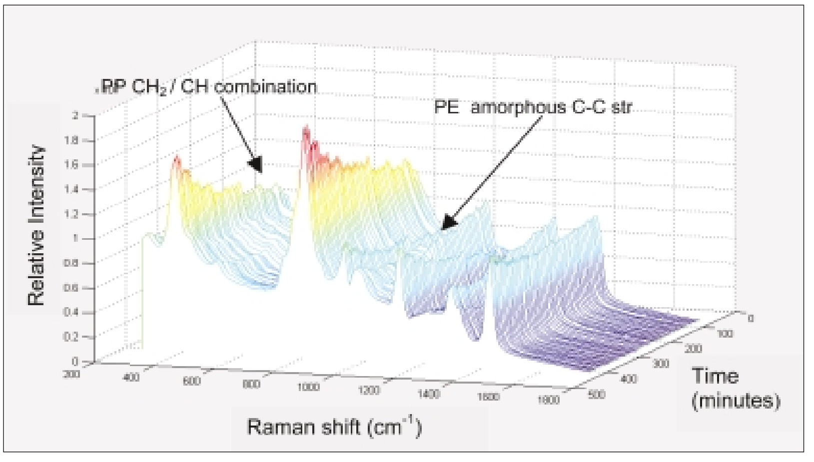

Figure 2. Real-time plot of the Raman spectra of a series of PP/PE blends acquired during extrusion.

The experimental set-up and spectral acquisition times for all spectroscopic techniques were chosen to achieve adequate resolution, sensitivity and signal-to-noise in an acceptable time frame in relation to the process dynamics.

On-line MIR and NIR spectra of the PP/PE blends were collected using a Dynisco–Kayeness infrared on-line spectrometer (IROS) system. Polymer was drawn from the extruder using a gear pump into a temperature- and pressure-controlled flow cell with adjustable pathlength. This process incurs a seven-minute time delay due to residence time of the polymer in the transfer line.

In-line transmission NIR spectra of the blends and copolymers were acquired across the melt flow using two-fibre optic transmission probes (Axiom Inc.) with sapphire windows allowing optical access through the sample. The probes are inserted into a 38 mm extruder section and intrude into the melt stream with a variable pathlength of 1–11 mm. Figure 1 is a 3-D spectrum showing in-line NIR spectra acquired during extrusion of a series of PEVA copolymers with increasing VA content.

In-line Raman spectra are collected using a Holoprobe integrated Raman spectroscopy unit (Kaiser Optical Systems Inc.) with a 785 nm laser and CCD detector. The melt is analysed using a flush mounted single in-line process probe with sapphire window. Figure 2 is a 3-D plot acquired real-time from the melt during extrusion of a series of PP/PE blends in 10% increments from 100% PP to 100% PE.

In-line fluorescence spectroscopy has being implemented onto a processing line for monitoring of low additive concentrations during polymer melt extrusion. Fluorescence spectra are recorded using a Perkin-Elmer LS50-B luminescence spectrometer coupled by fibre optics to an in-line fluorescence probe. Fluorescence has been applied as a technique for monitoring residence time distributions during melt extrusion by introduction of a fluorescent tracer into the melt.[8]

The use of fluorescence spectroscopy as a method for in-line measurement of melt temperature profiles is currently being investigated using temperature dependent fluorescing molecules doped into the melt in very low concentrations (typically 10 ppm).

Summary

Development of robust in-line high temperature and high-pressure probes and fibre optics, as well as analytical instrumentation, has paved the way for the use of spectroscopic techniques as tools to monitor polymer production processes in an industrial environment.

The production of new software allows real-time acquisition and manipulation of spectra during a process. Chemometric techniques can be applied to produce robust calibration models for quantitative analysis of polymer melt composition.

Process spectroscopy allows us to obtain more detailed molecular specific understanding of polymeric materials and any molecular changes which occur during processing. Monitoring of trends or component composition during a process allows evaluation as to whether a process is, in fact, under control. This will potentially allow closed loop control by use of specific measurements of material properties or process variables.

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