

Vibrational spectroscopic and ultrasound analysis for the in-process monitoring of poly(ethylene vinyl acetate) copolymer composition during melt extrusion

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Over the last decade, the demands for higher through-put in production, process optimisation and quality control in the polymer manufacturing industry has led to the implementation of a wide range of process analytical technologies. Techniques such as near-infrared (NIR) spectroscopy, Raman spectroscopy and ultrasound have become indispensable analytical tools for in-process monitoring allowing a molecular specific understanding of material characteristics, rheology and process trends. This paper reports the combined application of these three analytical techniques for assessment of co-polymer melt composition in-line during single screw extrusion to an accuracy of 0.16 wt%. The work demonstrates monitoring and characterisation of a series of ethylene vinyl acetate (EVA) random co-polymers with varying vinyl acetate (VA) content ranging from 2.0 to 43.1 wt%. The sensitivity of each technique to changes in copolymer composition and its ability to acquire real-time process data has been determined. Robust multivariate calibrations suitable for real-time predictions of VA content during processing have been developed and tested.

Introduction

Over the last decade in-line monitoring of polymer production processes has become increasingly important in the polymer industry due to increased economic, legislative and environmental demands for consistent quality of polymeric products.¹ Conventional process control schemes based solely on in-line measurements of physical parameters such as melt temperature and pressure are often unable to disclose all the variations in material properties, especially in the analysis of complex polymer systems.² The combined application of a range of process analytical techniques for *in-situ* physical property and molecular spectral characterisation is necessary to provide improved process understanding, control and optimisation. When implementing any process measurement minimising data acquisition time, whilst maintaining sufficient signal-to-noise ratio and resolution, is an also significant objective.³

Recent development of fibre optic technology, process-oriented spectroscopic instrumentation and robust probes has allowed a range of molecular based measurements to be taken from the melt in a non-invasive manner providing selective and sensitive assessment of process variables. Techniques such as mid-infrared (MIR) and near-infrared (NIR), Raman and UV-visible spectroscopies have been individually applied for molecular and morphological characterisation of a range of polymer melt systems during extrusion.^{4–8} However, very few comparative studies based on simultaneous process monitoring of component composition have been published in the literature.^{9–13}

This paper presents results from the implementation of a range of analytical techniques for in-line monitoring of the composition of a series of industrially produced polyethylene vinyl acetate (EVA) copolymers during melt extrusion. EVA random copolymers are produced by the free radical copolymerisation of ethylene and vinyl acetate (VA) under high pressures and temperatures. These versatile copolymers are produced with a wide variety of chemical and physical properties for a range of industrial applications, strongly related to the VA content.¹⁴ Characteristically, EVAs containing 0–18 wt% VA are used to produce polymer films whereas those containing greater than 20 wt% VA are used to produce adhesives and coatings. Due to the strong correlation between co-monomer content and product properties, it is essential that the content of VA is accurately and continuously monitored for quality control purposes.¹⁵

There are several standard off-line methods for determination of VA content in EVA copolymers, including titrimetric analysis, ¹H NMR, thermogravimetric analysis (TGA) and FTIR analysis.¹⁶ Raman and reflectance NIR spectroscopies in conjunction with chemometric analysis have also been used for off-line evaluation of the VA content in EVA copolymers in the solid phase.^{17,18} More recently, a number of in-line studies of EVA composition have been conducted using in-line NIR,^{19,20} and Raman spectroscopies.^{21,22} Little research has been published on ultrasonic velocity measurements of EVA. Although transient effects of polymerisation of VA homopolymers on ultrasonic velocity has been described,²³ no data are available on the relationship between ultrasonic velocity and VA content in EVA copolymers.

In this current publication, Raman spectroscopy, transmission Fourier transform near-infrared (FT-NIR) spectroscopy

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and ultrasound velocity measurements have been simultaneously applied for assessment of the VA content of a series of EVA copolymer melts during sequential extrusion. The ability of the spectroscopic techniques to acquire rapid, real-time data from the process has been investigated and multivariate analysis techniques have been applied for production of calibration models for determination of melt composition during processing.

Experimental

Raw materials

A series of seven commercial ethylene vinyl acetate random block copolymer resins (AT Plastics Inc.) with varying VA comonomer contents were used for the following research (Fig. 1). The vinyl acetate content present in each of the copolymers was determined to be 2.0, 7.3, 9.0, 17.1, 27.8, 34.2 and 43.1 wt% respectively, through thermogravimetric (TGA) analysis (RAPRA Technology Ltd) of the samples.

Extrusion

The copolymers were sequentially extruded from 2.0 to 43.1 wt% VA in a Betol 38 mm single screw extruder operated at a set screw speed of 15 rpm and a die set temperature 200 °C. Spectroscopic and ultrasonic probes were implemented into dies attached to the end of the extruder barrel. An infrared melt temperature sensor (Dynisco MTX series) and a Dynisco PT422A melt pressure transducer (0–500 psig) were used to monitor melt temperature and pressure in the die, respectively (Fig. 2).

Analytical techniques

Near infrared spectroscopy

In-line transmission FT-NIR spectra of the EVA melt samples were acquired during processing using an IROS100 FTIR system equipped with high temperature fibre optics attached to two FCP-080 through transmission NIR probes (Axiom Analytical Inc).^{11,12} The probes were inserted into a 38 mm die section located directly after the extruder barrel. Analysis of the melt was conducted at an optical pathlength of 1 mm, with the probes intruding into the melt section. Spectra were collected in the wavelength range 1600–2000 nm. Data were acquired using Orbital Science Corporation/Analect FTIR PC80 software and exported to Grams/32I (Galactic Industries

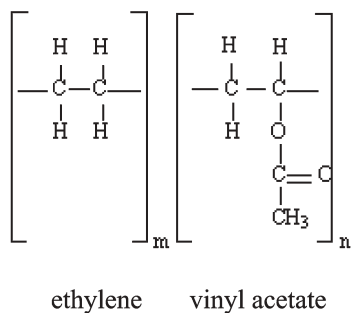


Fig. 1 Structure of ethylene vinyl acetate (EVA) copolymers.

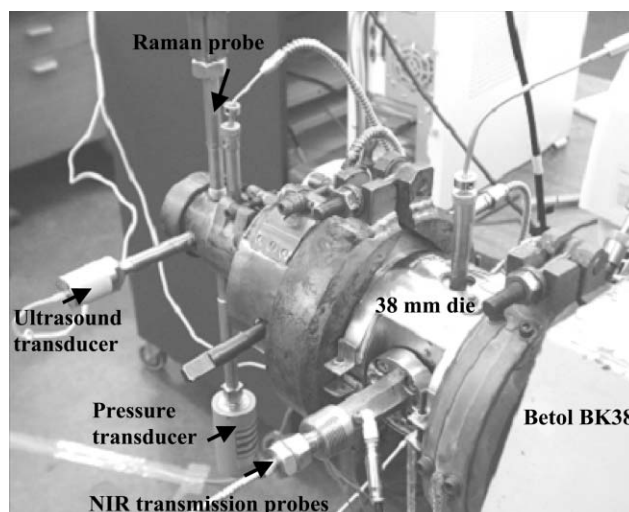


Fig. 2 Experimental set-up of Raman, FT-NIR, Ultrasound, temperature and pressure probes in the Betol 38 mm single screw extruder during in-line analysis of EVA copolymers.

Corp.) for further data manipulation and production of Partial Least Squares (PLS) regression models. NIR spectra of the copolymers acquired simultaneously with Raman scatter and ultrasound velocity measurements were scanned at a nominal resolution of 4 cm⁻¹ and averaged over 32 accumulations, resulting in an overall scan time of 1 min. The scanning period was chosen to give adequate sensitivity and signal-to-noise ratio within an acceptable time frame for the extrusion process.

Two independent experiments were conducted for determination of the effect of a reduction in NIR data acquisition time on the accuracy of the subsequent PLS calibration models. Decrease in acquisition time during extrusion was achieved by two methods, whilst maintaining the wavelength range over which the spectra were acquired. The first data series were acquired over a 15 s time period achieved by averaging each spectrum over 8 scans (rather than the original 32 scans) at a resolution of 4 cm⁻¹. The second series were acquired over a shorter 10 s duration by reducing the spectral resolution to 8 cm⁻¹, and the number of scans to 8.

Raman spectroscopy

Melt spectra were collected using a HoloProbe RXN-2 analyser (Kaiser Optical Systems Inc.) integrated Raman spectroscopy unit (785 nm laser and CCD detector) interfaced with the extruder by a fibre optic in-line process probe implemented into a standard 1/2" UNF transducer port.²⁴ The probe was located in a 15 mm die head on the end of the extruder where non-invasive measurements were acquired from the melt. In all cases the cosmic ray filter facility of the software was engaged for removal of noise spikes from the spectra. Commercial software (Grams and HoloReact) was used to process spectral data and chemometric models of the data were created in Grams PLSIQ.

Scans of the melt acquired alongside FT-NIR and ultrasound measurements, were collected every minute, each scan comprising one accumulation over a 28 s exposure time.

A series of independent experiments were conducted for assessment of the effect of Raman acquisition time on measurement accuracy. In-line Raman spectra of each copolymer were acquired from one accumulation over exposure times of 6 s and 1 s producing overall cycle times of 15 and 5 s, respectively.

Ultrasound transit time

Ultrasonic measurements were made from the melt using instrumentation unique to Bradford, comprising of an ultrasonic pulser-receiver (Panametrics 5900), a sampling digital oscilloscope (LeCroy 9350AM) and automated process monitoring and analysis software.^{25,26} Data from the pulser-receiver were sampled using the oscilloscope at a frequency of 1 GHz and converted to form an array of voltage values representing the magnitude of the received sound wave, and time values calculated from the known trigger time and sampling frequency. Data were acquired from the melt using custom-designed high temperature 3.5 MHz narrow band longitudinal wave transducers mounted directly opposite one another on wave-guides that were aligned flush with the die wall. This work concentrated on ultrasonic 'time of flight' (also called transit time) measurements which are related to the velocity of the acoustic signal through the polymer. Measurements were made across the melt, where the die internal diameter at the point of measurement was 15 mm. From the voltage–time waveform array, a measurement of the signal transit time was taken. This was the total time taken for the ultrasonic wave to travel through both transducers and the polymer melt, and is therefore related to the sound wave velocity. Continuous monitoring of the transit time was undertaken every second during extrusion of the copolymers.

Results and discussion

In-line NIR spectroscopy

The NIR wavelength region, 1600–2000 nm, contains the first overtone bands of the C–H stretching modes and second

overtone of the carbonyl stretching vibrations. Incorporation of further VA into the copolymers (with corresponding decrease of the ethylene content) results in a decrease in the intensity of the bands at 1728, 1764 nm, related to C–H stretching overtones of the ethylene group (Fig. 3). An increase in VA content also leads to an observed increase in the intensities of features at 1682 and 1938 nm ascribed to the first overtone of the C–H stretch and the second overtone of the carbonyl stretching mode of the VA monomer, respectively.¹⁹

Twenty spectra of each blend acquired during extrusion (1600–2000 nm) were used with the corresponding known VA content values (determined by TGA analysis) to produce a training data set for chemometric analysis. A PLS model of the data was constructed for accurate calibration of the VA content using spectra pre-processed by multiplicative scatter correction, which was found to be an effective method for removal of baseline fluctuations observed in the data.²⁷ The calibration required five factors (loading vectors) to fully model the variation in the spectral data set where the first two factors of the model were responsible for modelling of 99.7% of the variance in the NIR data. Analysis of the PLS loading vectors and scores for the model indicated that the three remaining factors were necessary to model the variation in background observed in the NIR spectra during extrusion of the copolymers ascribed to the changes in viscosity and optical clarity of the samples.¹¹ The standard error of calibration (SEC) for the model was calculated to be ± 0.164 wt% VA (1σ) determined from cross validation of the training spectra with the model itself. A plot of the actual VA content of the EVA samples against those predicted by the five-factor model (Fig. 4) showed excellent linear correlation ($R^2 = 0.999$) of the values.

Validation of the PLS model was conducted by calculation of the accuracy of the model for the determination of the composition of a series of independent copolymer spectra (ten spectra per melt sample) acquired in-line during a different extrusion run. The standard error of prediction (SEP) was determined to be ± 0.187 wt% VA (to 1σ). The close agreement between this prediction error and the SEC value indicates the

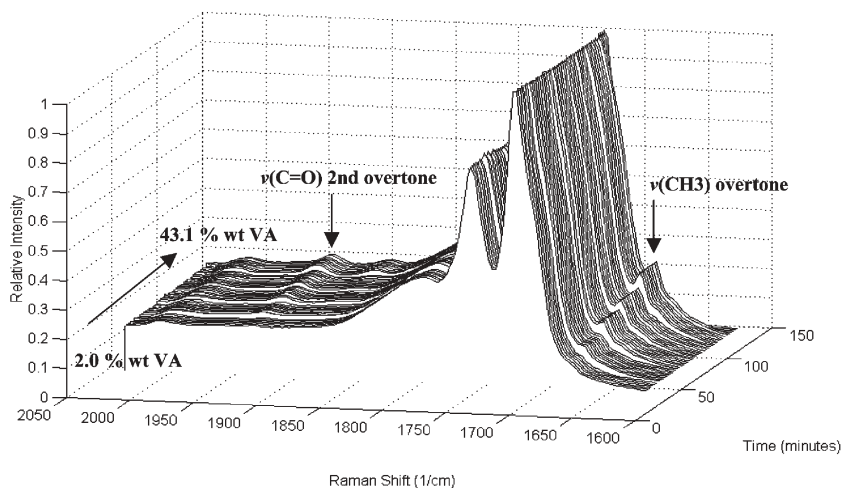


Fig. 3 Change in NIR spectra of the EVA samples (1 mm path length, 32 scans, 4 cm^{-1} resolution) with change in VA content during sequential extrusion from 2.0–43.1 wt% VA.

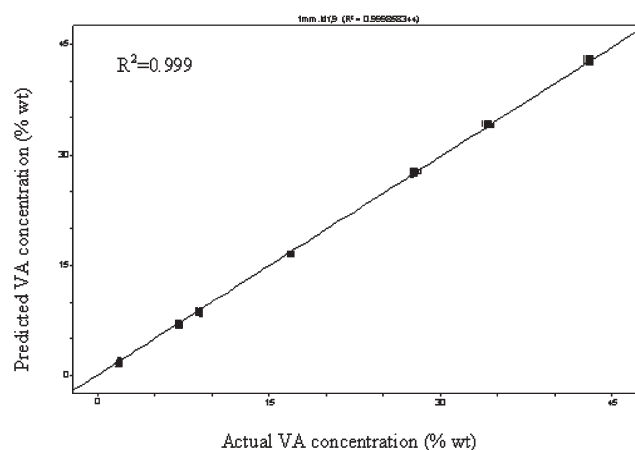


Fig. 4 Actual *versus* predicted VA concentrations for 5-factor PLS model of FT-NIR spectra.

robustness of the model for determination of the VA content of independent data sets.

PLS regression of the NIR spectra acquired over 15 s and those over 10 s both produced 5 factor models with calculated SEC values for each calibration of 0.17 and 0.18 wt% VA respectively (Table 1). The results presented in the table show good agreement between the errors calculated for each model and indicate that decreasing the overall scan time, by decreasing the spectral resolution and number of scan accumulations, does not significantly reduce the accuracy of the calibrations for determination of EVA melt composition (within the ranges studied). This is a consequence of the broad features and good signal-to-noise ratio of the FT-NIR spectra acquired at a 1 mm optical pathlength.

In-line Raman spectroscopy

A stack plot of the in-line Raman spectra acquired during processing from EVA melt samples of several VA contents are presented in Fig. 5. Significant increases in the intensity of the features associated with the vibrations of the VA co-monomer, especially the O=C=O deformation band at 630 cm^{-1} and the carbonyl stretching vibration at 1740 cm^{-1} are observed with increasing VA content.

Decrease in intensities of the features at 1440 and 1302 cm^{-1} associated with CH_2 bending and twisting modes of the ethylene group, were also observed with rising VA content.

The integrated area of the O=C=O deformation band at 630 cm^{-1} was used to monitor the changing VA content of the copolymers during sequential extrusion (Fig. 6). The plot shows clear distinctions between each copolymer grade as well as detecting material change-over. Changes in the intensity of

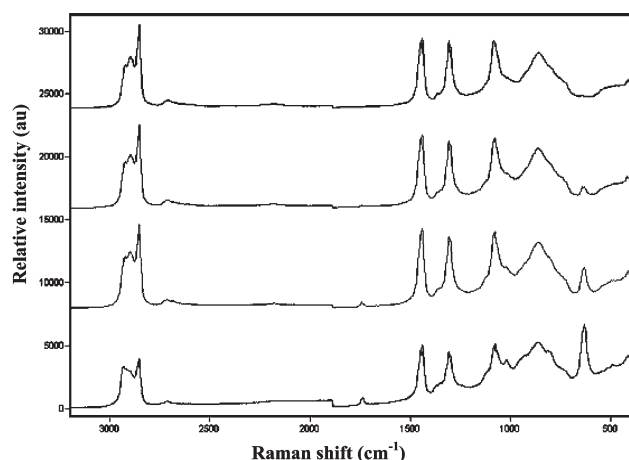


Fig. 5 Raman spectral stack plot ($3100\text{--}500\text{ cm}^{-1}$) of EVA copolymer melts containing (from the top) 2.0, 9.0, 27.8 and 43.1 wt% VA.

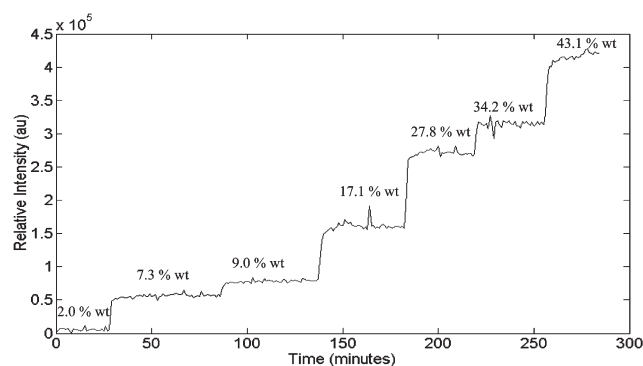


Fig. 6 Change in the integrated area of the O=C=O deformation mode at 630 cm^{-1} with time during sequential extrusion of the EVA copolymers from 2.0–43.1 wt% VA.

the band were observed during nominally steady state extrusion of some of the polymer samples. These were ascribed to the presence of residual material from previous grades in the barrel, fluctuations in sample fluorescence and changes in detector response during scanning.

A PLS regression model was constructed using a training data set comprised of twenty training spectra of each copolymer melt and the actual VA content values. The optimum model for determination of VA content was created from linear baseline corrected Raman spectra using the wavenumber region $1800\text{--}500\text{ cm}^{-1}$. The calibration required an optimum number of three factors to successfully produce a robust model of the variation in the melt spectra of the EVA series. The first factor corresponded to variations in spectral features with the change in VA content in the samples and the subsequent two factors were required to fully model the variations in the fluorescence background of the spectral data.¹¹

Linear baseline correction was determined to be the most effective method of removing the fluctuations in fluorescence background. The SEC was calculated to be $\pm 0.30\text{ wt}\%$ VA (to 1σ) by cross validation of the training data which was in good agreement with the corresponding SEP ($\pm 0.38\text{ wt}\%$ VA).

Table 1 Change in the calculated errors for the PLS models constructed from FT-NIR spectra of the copolymers with alteration in scan time

Scan number	Resolution/ cm^{-1}	Scan time/s	SECV (wt% VA)	SEP (wt% VA)
32	4	60	0.164	0.187
8	4	15	0.175	0.195
8	8	10	0.183	0.201

PLS regression models were calculated for copolymer spectra acquired in-line, during processing over 15 and 5 s acquisition times. Both calibrations required an optimum number of three factors to fully model the data and the subsequent SEC values were calculated to be 0.45 and 1.56 wt% VA respectively (Table 2). These values indicate that a reduction in scanning time to 15 s does not significantly affect the accuracy of the calibration for prediction of the composition of the EVA melts.

However, further reduction of the scan time to 5 s shows a more substantial rise in the calibration error reflected in the reduced signal-to-noise ratio observed in the raw spectral data. A 15 s scan time would be suitable for analysis of the melt composition providing a high level of accuracy as well as approaching real-time data acquisition. A more dynamic

process such as reactive extrusion or the more extreme case of injection moulding would further require a trade-off between accuracy and response time.

Ultrasound transit time

Ultrasound transit time measurements were acquired simultaneously with Raman scattering and FT-NIR measurements in-line during sequential single screw extrusion of the copolymers. Fig. 7 shows detail of an actual waveform as displayed on the digital oscilloscope for transit time determination. The data acquisition system is programmed to search the array and look for a voltage peak above a user-defined threshold, before identifying the next point in time at which the voltage values pass zero. The time at which the voltage crosses zero following a pre-selected threshold is output as the transit time.

Variation in ultrasonic transit time with increasing VA content is shown in Fig. 8. As the VA content is increased, the transit time rises due to changes in density and elastic moduli of the polymeric material. The figure also illustrates the inconsistent variation in melt pressure occurring during extrusion as a consequence of the non-linear change in melt index throughout the samples. A least squares regression calculated for ultrasound transit time against VA content produced a linear fit ($R^2 = 0.973$) with a calibration error of 2.82 wt% VA.

The errors associated with the prediction of VA content are attributed to the effect of pressure changes on the transit time. In addition a regularly occurring fluctuation could be observed in the transit time, related to the dynamics of the extruder and possibly to melt temperature.

The prediction error could potentially be reduced by off-line calibration of transit time with changes in temperature and pressure for each of the EVA samples, and subsequent modification of the in-line data. Application of the ultrasonic technique would then necessitate simultaneous accurate

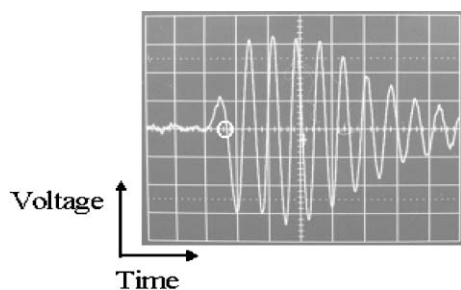


Fig. 7 Example of ultrasound transit time measurements during EVA extrusion.

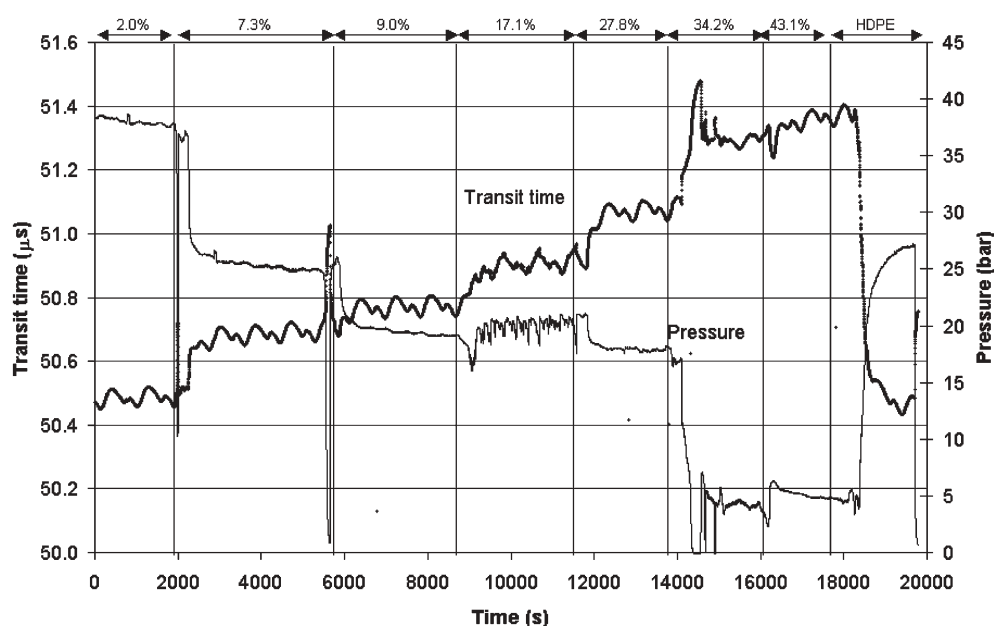


Fig. 8 Change in ultrasound transit time and melt pressure during sequential EVA extrusion.

measurement of temperature and pressure in the die during extrusion.

Comparison of the techniques

All three analytical techniques were sensitive to changes in melt composition with the change-over between resins and steady state extrusion of each sample clearly visible in all the data. FT-NIR has been shown to be the most sensitive technique to alterations in VA content of the EVA copolymers during melt extrusion.

A comparison between the response of the ultrasonic transit time and Raman measurements to changes in copolymer content during extrusion is shown in Fig. 9. Both techniques respond well to the changes in VA content and are in excellent agreement with one another as to when the changes occur.

The ultrasound detects the changes in material content slightly earlier than the Raman data, as a consequence of the faster scanning times adopted by the velocity measurements. Anomalies observed in the ultrasound data, related to changes in measured melt pressure were not seen to affect the Raman scattering intensity indicating that the spectroscopic technique is more stable to fluctuating process conditions. However, problems were encountered in the Raman technique, with a fluctuating background fluorescence observed in the EVA spectra, ascribed to the presence of additives, impurities and degraded material in the melt. The FT-NIR absorbance data were observed to be more stable than the Raman intensity measurements during extrusion although changes in the baseline intensity of the NIR spectra between samples were witnessed as a consequence of the observed change in optical clarity of the polymer with increasing VA content.

PLS models produced from the FT-NIR and Raman spectra acquired over shorter scan times showed that spectral data could be acquired over rapid integration times without

significant effect on the associated errors of the calibrations of copolymer composition. Further reduction of the NIR spectral acquisition time can be achieved by a reduction in the wavelength region over which the data is acquired. However, care must be taken to ensure that the full region of the spectrum over which process changes are occurring is analysed, in order to extract all the information possible from the measurements.

From a process engineering perspective, the FT-NIR transmission technique currently adopted requires the use of process probes with non-standard fittings which are intrusive into the melt flow in order to achieve the required optical pathlength for analysis. The Raman and ultrasound techniques both use non-invasive probes with standard process fittings making them much more versatile for process measurements. Raman spectroscopy also only requires just a single probe for melt analysis which is often much easier to implement onto a process than two parallel probes.

Problems were encountered during processing of the copolymers containing high VA content due to the high melt flow indices/low viscosity of some samples making the polymers difficult to convey along the extruder and between the NIR transmission probes. Purging of these polymers from the screw and from around the windows of the probes also proved problematic.

Conclusions

In-line FT-NIR and Raman spectroscopic techniques have been used alongside ultrasonic transit time measurements for monitoring during single screw extrusion of a series of EVA copolymers. All three analytical monitoring techniques were found to be sensitive to the alteration in VA content. The spectroscopic and ultrasonic techniques provide excellent

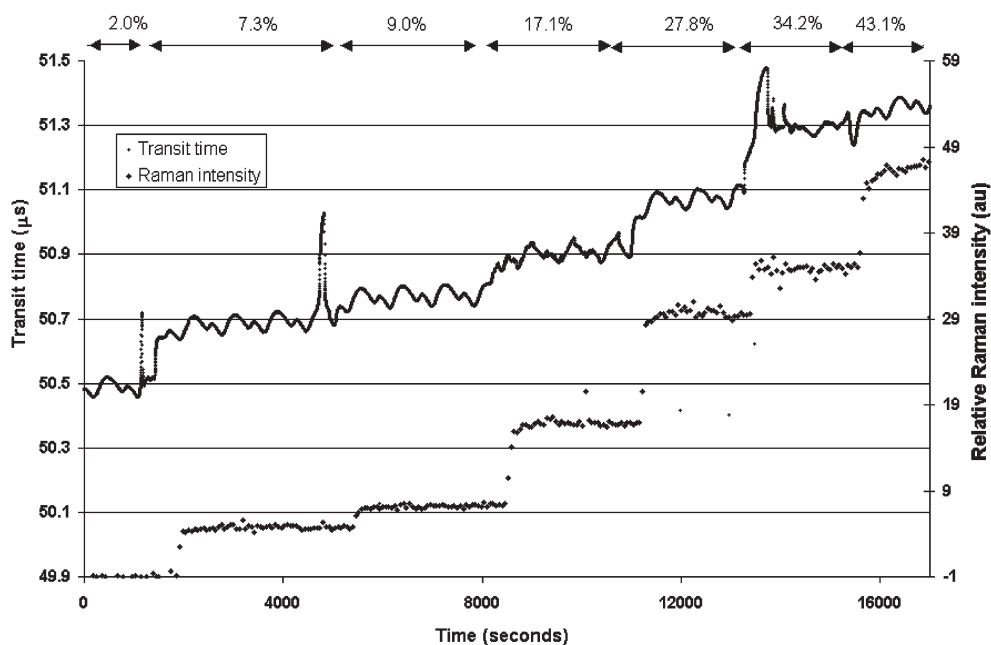


Fig. 9 Comparison of change in integrated Raman band area at 630 cm^{-1} and ultrasound transit time measurements with VA content during processing.

agreement regarding the transient changes of material, such as would occur in material changeover in extrusion. Ultrasonic velocity measurement provides an immediate assessment of bulk properties across the entire melt and is highly sensitive to changes in VA content of the copolymer resins, however a lot of noise was present in the transit time data due to the affects of changes in melt pressure and temperature during extrusion of the copolymers.

In-process near infrared and Raman spectroscopies have been shown to give good quality, high signal-to-noise ratio spectra of EVA melts in the extrusion process, at data capture rates as rapid as 5 s which are useful for real-time process monitoring. The stability of the spectroscopic measurements to fluctuations in processing parameters under nominally steady state extrusion conditions indicates the techniques suitability for in-line analysis. Although spectroscopic data collection is not as rapid as the ultrasound measurements, such techniques provide molecular characterisation of the melt as opposed to the bulk mean continuum measurements gained using ultrasound.

In-line prediction of wt% VA content has been successfully conducted using all three techniques, where PLS regression has been successfully applied to both the Raman and FT-NIR data to build multivariate calibration models. FT-NIR has been shown to be the most sensitive technique to changes in copolymer composition during processing with errors calculated to be as low as 0.16 wt% VA for prediction of the VA content of flowing melt samples.

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