



In-process vibrational spectroscopy and ultrasound measurements in polymer melt extrusion

P.D. Coates^{a,*}, S.E. Barnes^a, M.G. Sibley^a, E.C. Brown^a, H.G.M. Edwards^b, I.J. Scowen^b

^a*IRC in Polymer Science and Technology, School of Engineering, Design and Technology, University of Bradford, Bradford BD7 1DP, UK*

^b*Department of Chemical and Forensic Sciences, University of Bradford, Bradford, UK*

Received 19 March 2003; received in revised form 6 May 2003; accepted 8 May 2003

Dedicated to Prof. Ian M. Ward on the occasion of his 75th birthday

Abstract

Spectroscopic techniques have the potential to provide powerful, molecular-specific, non-invasive measurements on polymers during melt processing operations. An exploration is reported of the application and assessment of sensitivity of in-process vibrational spectroscopy—on-line mid-infrared (MIR), on-line near-infrared (NIR), in-line NIR and in-line Raman—for monitoring of single screw extrusion of high-density polyethylene and polypropylene blends. These vibrational spectroscopic techniques are compared with novel in-line ultrasound velocity measurements, which were acquired simultaneously, to assess the sensitivity of each method to changes in blend composition and to explore the suitability for their use in real time process monitoring and control.

© 2003 Elsevier Ltd. All rights reserved.

Keywords: In-process vibrational spectroscopy; Polymer melts; Raman spectroscopy

1. Introduction

1.1. In-process measurements

The use of measurements to characterise materials during processing is increasing, with analytical techniques rapidly developing from conventional laboratory-based methods to real time tools for process diagnostics and control. Polymer melts are history-dependent materials, for which the current responses depend on the stress, strain, strain rate and temperature history of the melt [1–4]. Standard ‘off-line’ (i.e. laboratory) assessments of polymer melt properties may therefore be misleading, particularly if the off-line tests involve significantly different histories from those encountered in processing, or if the polymer molecular features change in the tests. For example, melt residence times in a standard capillary rheometer, used to characterise the shear rheology of a melt, are typically more than 5 min, whereas typical process melt residence times in an extruder are around 1 min. If the polymer is affected physically or chemically by dwell time at a given temperature, (e.g. PET

and many other engineering polymers) it may be adversely affected during the off-line test, so that the material tested is not the same as that processed [2–4]. Of particular relevance to control of manufacturing processes, are also: (i) the representative nature of the test sample—off-line tests are necessarily limited to extremely small amounts of a material which may not be typical of the bulk of the material being processed and (ii) the total time taken to make measurements—this may typically be of the order of hours, by which time tonnes of material whose quality is being sampled may have been processed.

In-process monitoring aims to address these concerns, to provide an accurate, preferably ‘real time’ assessment of specific polymer properties, such as shear or extensional rheology, or composition. In addition, in-process monitoring can provide a sensitive indicator of stability of the process, including batch-to-batch variation [5,6], and as such can provide the basis for meaningful Statistical Process Control or other statistical assessments of process variation.

There are three main drivers for in-process measurements on polymer melts, namely to obtain data for:

- *scientific understanding of particular features of the material*, e.g. studies on how molecular topology

* Corresponding author. Fax: +44-1274-234-505.

E-mail address: p.d.coates@bradford.ac.uk (P.D. Coates).

influences bulk rheology in process-relevant flows, or spectroscopy used to assess molecular feature changes in a polymer during processing;

- *modelling of real process flows*, e.g. development of rheological models and constitutive equations for use in computer modelling of die flows, cavity filling, and validation of process modelling;
- *process trend monitoring*, to evaluate if a manufacturing process is under control, with potential for closed loop control, by use of specific property or process variable measurements.

The range of measurement techniques which can be applied to polymer melts include: rheometric, optical, ultrasonic, electrical and spectroscopic (IR, UV, dielectric and NMR) [1]. These are used for measurement of flow properties, polymer structure, morphology and composition, additive concentration, dimensions, appearance, colour and consistency of production. In-process measurements may be on-line or in-line. On-line measurements [2–4] require polymer melt to be sampled from the main process (with relatively small sample volumes compared with those in the main process), often using gear pumps (adding strain and temperature history), with the chosen measurement being made on the sampled material in equipment adjacent to the processing line—normally an extruder. This incurs a delay time, and perturbation of the process by removal of melt (some devices return the melt to the process line, so the total flow rate through the process is not affected), and also raises issues of how representative the small sample of melt is of the whole process flow. This is particularly the case when the melt sample stream has to be taken from close to the wall of the main processing equipment. However, the on-line measuring system can allow conditioning of the sample, to provide consistency of the measurement environment; it is also possible to undertake tests similar to laboratory measurements, and over a range of conditions, i.e. multi-condition data can be generated for a single process flow. An example of an on-line device is an on-line capillary rheometer, where strain rates are controlled by a gear pump and chosen capillary die geometry; the sample melt temperature may be controlled. On-line measurement techniques in current use include on-line rheometers (OLRs), [7], essentially providing shear flow measurements. Assessments of extensional behaviour have been inferred from entry pressure measurements [3] and rheo-optical studies [8] while other in-line techniques include mid and near infra-red spectroscopy [9,10], are mainly concerned with molecular features and composition. UV -visible and fluorescence spectroscopy have found application for the assessment of additive concentration and for residence time distribution measurement.

In-line measurement aims to obtain data from the main process flow, preferably without disturbing this flow (e.g. by using sensors which are flush-mounted with flow channel walls). This may allow a much greater proportion of the

melt to be sampled; but tends to give only a single point measurement, under the pertaining process conditions. The actual sampling volume (its location in the process flow stream and its actual size) are important yet often poorly defined for in-line measurements.

Current in-line devices are used for rheometric, optical (including colour and composition), dielectric, ultrasonic, near infra-red, UV, and conductance measurements [1]. A specific example of is an in-line shear rheometer [12–14], where shear rate is decided by process flow rate; melt temperature is decided by process conditions, so the measurement is normally non-isothermal.

In-process measurements on polymers are normally bulk measurements—for example, the on-line and in-line rheometers referred to above. In contrast, infrared and Raman spectroscopy can provide information on bond vibrations within molecules. Molecular vibrations produce characteristic spectral features at different wavelengths throughout the spectral range, which can be individually identified and assigned. These two spectroscopic techniques provide complementary information to one another, relating to the chemical composition of the polymer and the structure of the skeletal backbone. In general, such spectroscopy techniques have been predominantly used to study solid polymers—including extensive studies of molecular orientation by Ward and Bower [15–17], and also Cole and Aji [18].

However, in view of the need to enhance the control of manufacturing processes, such as polymer melt processing, the application of spectroscopic techniques to polymer melts is appealing—but not without practical difficulties. Some of the studies of the use of these techniques to characterise polymer melts during processing are being undertaken confidentially in industry, and very few references to this area of research are available in the literature. However, many off-line studies of the vibrational spectra of polymers over various temperature ranges have been conducted to investigate recrystallisation processes, thermal degradation and hydrogen bonding [19]. In general, bands associated with order (for example crystallinity) disappear with melting, whereas bands associated with the amorphous state broaden due to changes in the molecular environment on melting. The recent development of fibre optic technology, process orientated spectroscopic instrumentation and robust process monitoring probes, has led to the implementation of in-process melt analysis, for example in the work of Fischer [20], Hansen [9,10] and our own laboratory [21].

The implementation of spectroscopic techniques to obtain real-time information about a process stream has also been adopted in a number of industries such as food analysis [22], petrochemicals [23], pharmaceuticals [24], and textiles [25]. In general, the application of spectroscopic techniques to polymer melts has been arguably more difficult, in part due to the pressures and temperatures encountered in processing.

In-line NIR spectroscopy has been reported for polymer composition measurement [9,26], for EVA copolymer composition monitoring and melt index correlations [10], and at-process Raman by Hansen for EVA composition [27]; UV fluorescence spectroscopy has been utilised as a method for determination of residence time distribution (RTD) during twin screw extrusion [11]. In our laboratory, on-line MIR was used successfully to monitor change in PP/PE blend ratios during single screw extrusion [21]—the initial studies for the more extensive work reported here—and fluorescence spectroscopy has recently been employed to monitor additive concentrations and RTDs in extrusion.

Ultrasound measurements (normally ultrasound velocity or transit time) have been available commercially for some years, for polymer product assessments such as extruded pipe wall thickness distributions. Process ultrasound measurements on melts have been explored recently by several laboratories (e.g. [28,29]), normally using transit times for longitudinal ultrasound waves. Signal attenuation can also provide useful information, but is more difficult to measure accurately. Shear waves may also be used to study process effects related to polymer solidification—melts will not sustain shear waves. Both bulk modulus and density affect ultrasonic velocity, and hence transit time. Change in material or process conditions (temperature and pressure) will consequently affect ultrasonic velocity; this effect has been reported in preliminary studies when polypropylene/polyethylene blend ratio were altered during extrusion [21].

1.2. Infrared spectroscopy

Vibrational excitation is achieved by illuminating the sample with a broad band source of radiation in the IR region of the electromagnetic spectrum (12,000–400 cm^{-1}). The MIR range from 4000 to 400 cm^{-1} contains fundamental vibrations, whereas the NIR range, 12,000–4000 cm^{-1} , contains overtone and combination band features. Vibrations of bonds with large dipole moments such as OH and CO are strongly IR active.

Experimentally, under steady system conditions, a logarithmic correlation can be made between concentration of chemical species and absorbance, A , using the Beer–Lambert law:

$$\text{Log } A = \epsilon cl \quad (1)$$

The coefficient ϵ is the molar absorption coefficient of the species under investigation and the sample concentration is represented by c at an experimental path length, l . For a particular material at constant path length, it is possible to directly correlate an alteration in the band absorbance intensity to a change in concentration.

1.3. Raman spectroscopy

The relationship between the signal intensity and species concentration is linear [30], but is also dependent on a

number of sample and equipment properties such as: refractive index of the sample, molecular environment, polarisation geometry of the exciting radiation and sensitivity of the detector. For this reason, the absolute Raman band intensity is not often used for quantitative analysis and instead the intensity of the spectral band of interest, is normalised to that of an internal standard [31]. This quantitation is particularly challenging for in-process measurement. Our laboratories also have extensive off-line Raman spectroscopy experience for polymers and a wide range of other materials [32].

1.4. Ultrasound

Longitudinal ultrasonic velocity responds to changes in bulk modulus and density. In-line measurements on polymer melts should therefore allow real-time detection of blend variation.

The velocity of propagation of an ultrasonic wave is a characteristic of a given material and of the waveform type, and can be calculated using the elastic constants of the material. The value of ultrasonic velocity changes with temperature and pressure related to variations in elastic moduli and density with these parameters [33]. Temperature and pressure effects are related for a given material.

The velocity of propagation of longitudinal waves (C_l) can be defined in terms of the bulk (K) and shear (G) moduli, and the density (ρ).

$$C_l = \sqrt{\frac{1}{\rho} \left(K + \frac{4G}{3} \right)} \quad (2)$$

Since shear modulus is relatively small for polymer melts in comparison with their bulk modulus, Eq. (2) is normally simplified for melts to:

$$C_l = \sqrt{\frac{K}{\rho}} \quad (3)$$

2. Experimental

2.1. Raw materials and blends

Spectroscopy is of particular value when monitoring molecular features, including process-induced changes. Here we use a blend of two polyolefins to provide model materials which simulate relatively large, known changes in the processed material, in order to assess the sensitivity of the in-process measurement techniques.

A high density polyethylene, HDPE BP 6007XA (BP Chemicals) and a polypropylene homopolymer, BASF Novolen N1102 M were employed. A series of PP/PE blends were made by tumble blending of weighed amounts of pellets at the required wt% ratio in 10 kg batches. The blends were extruded sequentially and the change in blend

ratio monitored. In the first series of experiments, sequential extrusion of blends was explored using the following blend ratios: 100 wt% PP; 50 wt% PP–50 wt% PE; 25 wt% PP–75 wt% PE; 15 wt% PP–85 wt% PE; 10 wt% PP–90 wt% PE; 5 wt% PP–95 wt% PE; 1 wt% PP–99 wt% PE; and 100% PE. Only on-line spectroscopy techniques were available for these blends. In the second set of experiments, blends were extruded sequentially in steps of 10 wt% from 100% PE to 100% PP, and both on-line and in-line spectroscopy techniques were available.

2.2. Equipment

2.2.1. Extrusion

On-line mid-infrared (MIR) and near-infrared (NIR), in-line NIR, and in-line Raman spectroscopy have been used to monitor changeover in blend concentration for the series of PP/HDPE blends which were extruded using a Betol BK38 38 mm single screw extruder at a set screw speed of 15 rpm and a die set temperature 200 °C. Figs. 1 and 2 show the experimental arrangement with Betol extruder with the on-line MIR/NIR rheometer attached, together with in-line ultrasound sensors. An infra-red melt temperature sensor (Dynisco MTX series) was used to monitor melt temperature in the die.

2.2.2. Infrared at-process spectrometers

A Dynisco-Kayeness Infra Red On-line Spectrometer (IROS) system was used: this was specially designed for our laboratory to have a replaceable FTIR system (Orbital Inc., now Hamilton Sundstrand), allowing either MIR or NIR measurements to be made. The IROS unit uses a gear pump to draw polymer from the extruder via a temperature

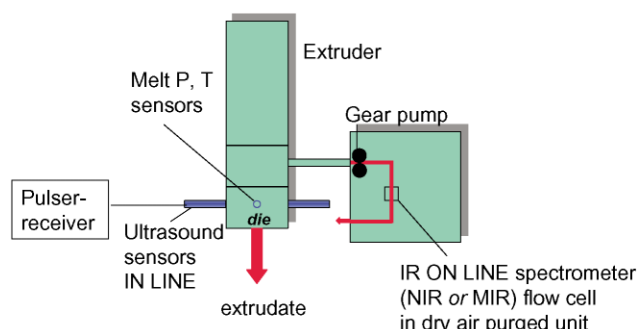


Fig. 2. Schematic diagram of the equipment shown in Fig. 1.

controlled transfer channel, into the adjustable gap IR cell, producing a continuous flow through the cell. This on-line measurement incurs a time delay of approximately 7 min at the set conditions (4 rpm gear pump, transfer line set temperature 230 °C, cell set temperature 200 °C) due to melt residence in the transfer line and fittings between the extruder and the measurement cell. The IROS sampling unit is purged with dried air (Whatmann system) to exclude moisture and carbon dioxide. It uses KBr beam splitters for MIR mode, and CaF₂ for NIR mode. It has an adjustable cell bypass, to allow melt flow to be diverted from the cell, so controlling pressure in the cell.

With the system air purged and a background spectrum taken, a spectral ‘sample’ was collated every minute during blend extrusion. For the MIR this comprised of 16 scans from 4400 to 400 cm⁻¹ at a resolution of 2 cm⁻¹, and in the NIR 16 scans from 12,000 to 4000 cm⁻¹ at a resolution of 4 cm⁻¹ were collected. These combinations of scan number and resolution were chosen to obtain adequate sensitivity in an acceptable time period in relation to the dynamics of the

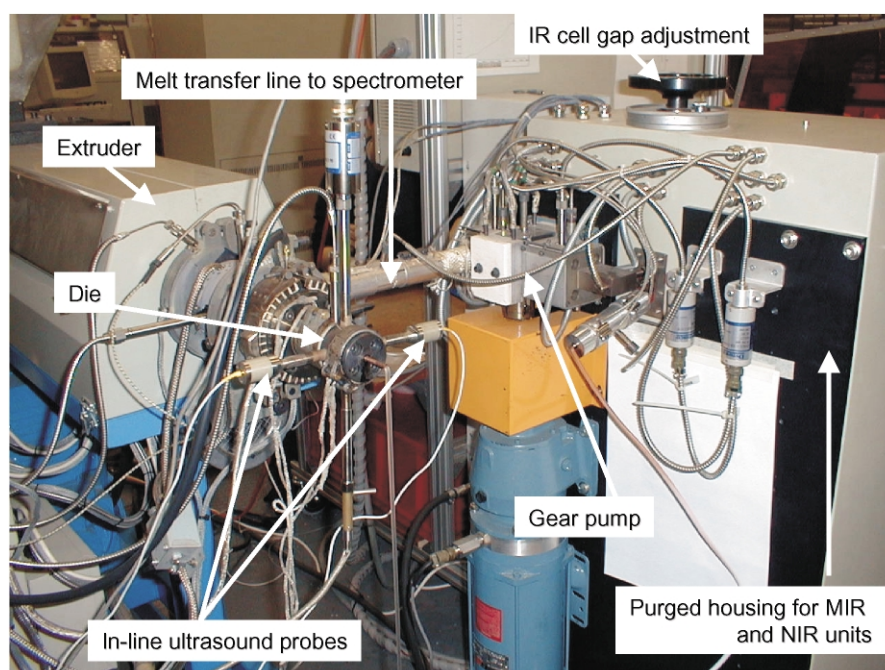


Fig. 1. Betol 38 mm single screw extruder with on-line IROS MIR and NIR spectrometer, and in-line ultrasound probes.

extrusion process. Fig. 3 indicates the difference in spectra when collecting at higher and lower resolution. For the relatively high resolution of 512 total scans, the signal to noise ratio is 22.6, but the collection time is over 30 min. For collection at the more practical 16 total scans, taking 1 min, the signal-to-noise ratio has fallen to four, but is still acceptable.

The IROS cell path length was set to the minimum gap of 0.01 mm for the MIR measurements, and for the NIR measurements was increased to 1 mm to enable the weaker overtone and combination features to be observed in greater detail.

In-line transmission NIR, in the range $8000\text{--}4650\text{ cm}^{-1}$ has also been explored in our laboratory, using a specifically designed (Axiom Inc.) stainless steel extruder section, 38 mm inner diameter, just prior to the die. This uses fibre optic through-transmission probes with sapphire windows, taking laser light from the IROS and signals directly to the IROS FTIR units. A variable melt path length at the fibre optic unit tips can be set mechanically, from 1 to 10 mm (using 1 mm spacers). The configuration is shown in Fig. 4. This experimental arrangement is clearly intrusive when used with the 38 mm diameter flow channel on the 38 mm single screw extruder, in order to allow sufficiently small path lengths to obtain adequate NIR signals. Too large a path length causes unacceptable signal attenuation.

In the experiments reported here, collated spectra comprised of 32 scans at a resolution of 4 cm^{-1} and a selected path length of 1 mm.

2.2.3. Raman process spectrometer

Spectra were collected using a Holoprobe (Kaiser Optical Systems Inc.) integrated Raman spectroscopy unit and an in-line process probe (Fig. 4). The flush mounted single probe provides both excitation and collection of signals. The system has a 785 nm diode laser and CCD detection of the Raman scatter. Scans of the melt were

collected every minute, each scan comprising of a 25 s exposure in the wavelength range 785–1080 nm. The scanning period was chosen to give adequate sensitivity within an acceptable time frame during the extrusion process. Spectra presented are plotted in Raman shift (cm^{-1}) from the incident radiation (785 nm). Commercial software (Grams and Holoreact) are used to process spectral data.

2.2.4. In-line ultrasonic monitoring

Ultrasound velocity is monitored to a high precision using a virtual instrument developed in our laboratories [29, 34–36]. This instrument comprises of an arrangement of custom designed high temperature 3.5 MHz narrow band longitudinal wave transducers mounted opposite each other on waveguides that align flush with the die wall (Figs. 1 and 4 show external views of this, and Fig. 2 a schematic diagram), an ultrasonic pulser-receiver (Panametrics); a 1 GHz sampling digital oscilloscope (LeCroy) and automated process monitoring and analysis software. Continuous real time monitoring of transit time was undertaken at a chosen frequency of 1 Hz. Measurements are made across the melt, where the die internal diameter at the point of measurement is 15 mm—as with NIR signals, too large a melt path length would lead to unacceptable signal attenuation. The melt then passes through a contraction zone, and ultimately exits via a rod die.

Ultrasonic velocity may be inferred from a measured transit time; this increases as ultrasonic velocity decreases, and vice versa. Data are presented in terms of the total transit time of the ultrasonic signal, through transducers and polymer melt. In addition, the peak height of the signal is monitored. A ratio of heights of two sequential peaks (the first after a single passage through the melt, and the second after three passages) can be used to calculate signal attenuation. This can also be related to process variations [36].

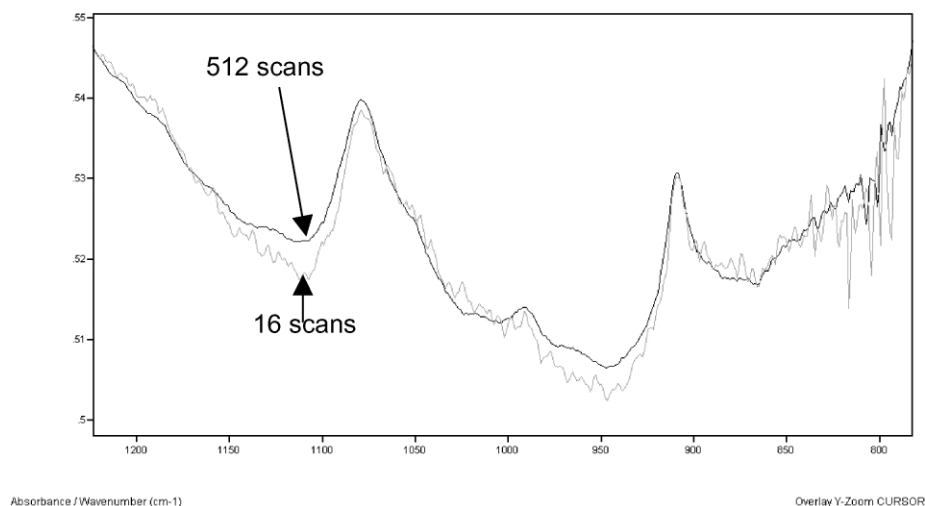


Fig. 3. Spectra for 100% HDPE collated from 512 scans and 16 scans respectively, at 2 cm^{-1} resolution.

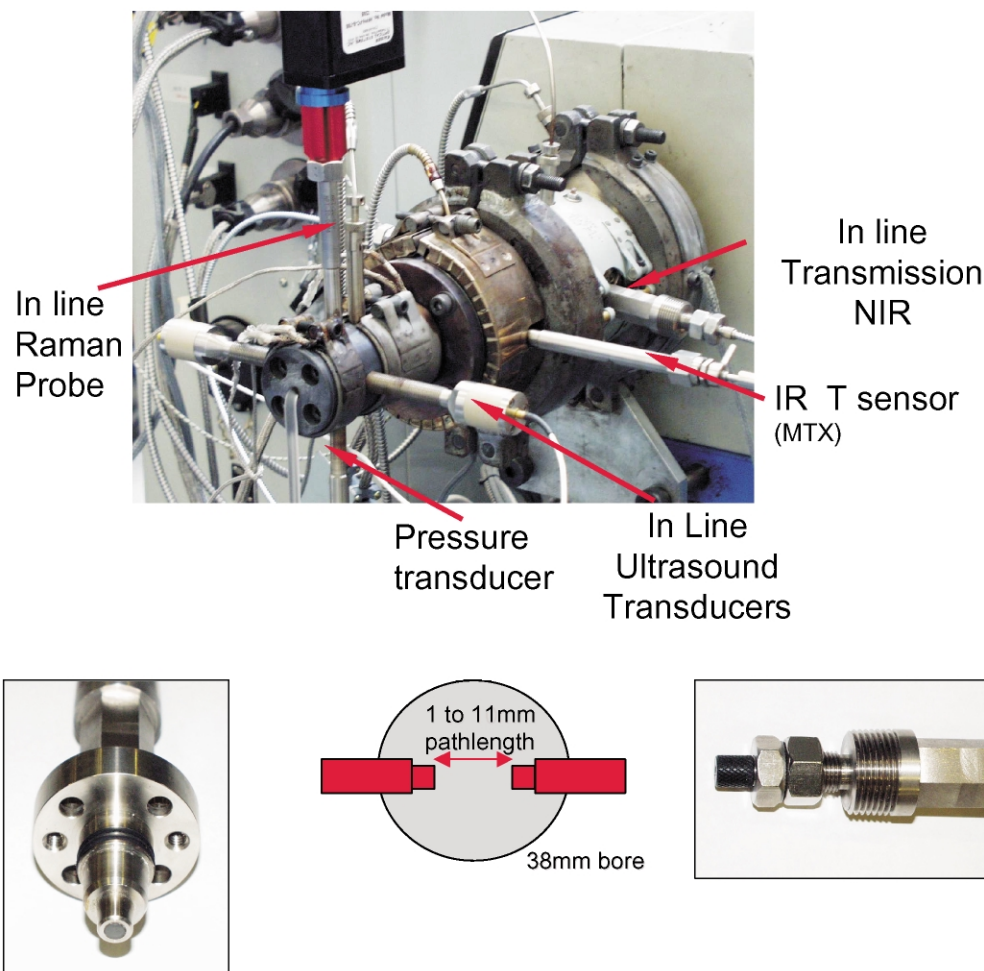


Fig. 4. In-line NIR spectroscopy arrangement and flush mounted fibre optic probes, for through-transmission measurements.

3. Results and discussion

3.1. Mid-infrared spectroscopy

The wavenumber range $1600\text{--}650\text{ cm}^{-1}$ contains the fingerprint region of the spectra of each blend (Fig. 5). Specific fundamental features can be assigned to vibrations occurring in each polymer and the intensity subsequently monitored. The intensities of key identifying features in the spectrum of PP, namely those at 1377 cm^{-1} (symmetric CH_3 bending), 1151 cm^{-1} (antisymmetric CH_3) and 972 cm^{-1} (CH_3 rocking) are observed to decrease as the wt% PP is reduced, whilst the 718 cm^{-1} peak relating to the polyethylene backbone stretching, is seen to increase in intensity with increasing PE concentration.

Fig. 6 is a 3D plot of on-line MIR spectra showing typical changes in peak intensity during extrusion of the PP–PE blends, here for a step in blend ratio from 100% PP to 25 wt% PP:75 wt% HDPE. Using the Beer–Lambert law a calibration plot can be constructed to show the relationship between blend concentration and intensity for each peak (Fig. 7).

The most sensitive response to change was observed for the 1377 cm^{-1} peak. The apparent sensitivity of this measurement to change in wt% PP is indicated by the slope of the line, which is approximately $-0.017\text{ abs units/wt\%}$. In practice, ~ 0.1 absorbance units resolution might normally be expected in IR spectroscopy, which indicates that a 1 wt% change in blend will not be resolved by this technique.

3.2. On-line near-infrared

Blend changes were also observed in the NIR region, in limited experiments, specifically for the first overtone/combination features present between 6100 and 5150 cm^{-1} . Fig. 8 shows the features observed for each blend, indicating intensity changes of each feature with change in blend ratio. The features in the NIR are fewer and broader than the fundamental peaks in the MIR. Problems with overlap due to the increased width of the features were also encountered, however change in peak intensity could still be evaluated and associated with blend changes.

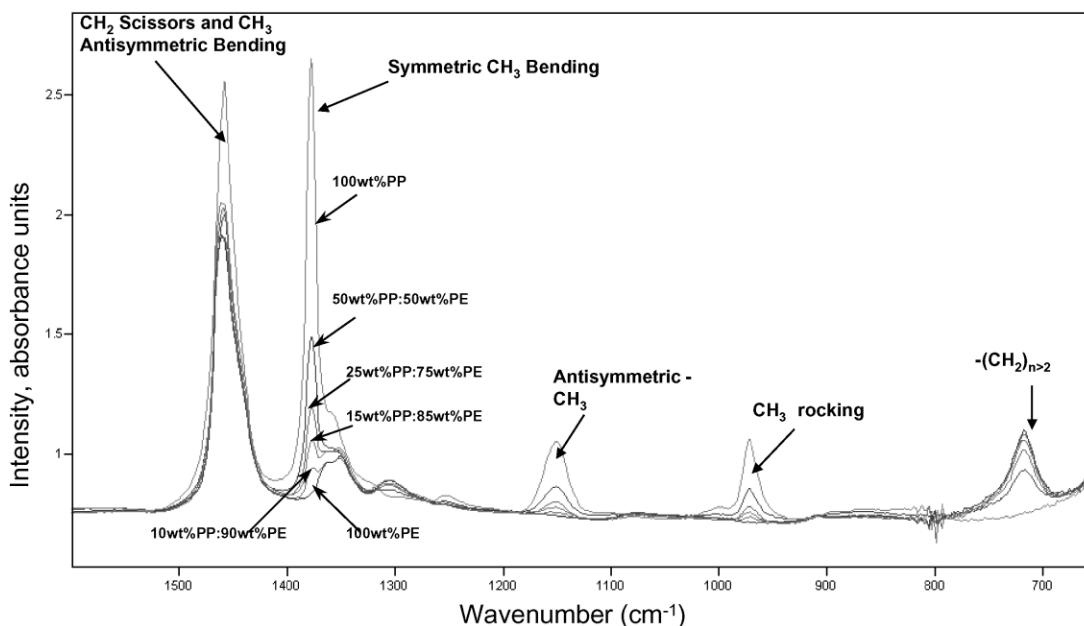


Fig. 5. On-line MIR spectrum of PP–HDPE blends.

3.3. In-line NIR

Fig. 9 shows results from initial experiments for in-line NIR measurements for sequential extrusion, changing from 100 wt% PP to 50 wt% PP:50 wt% PE, then to 100 wt% PE. The results correspond with those obtained for the on-line NIR. As noted for the on-line NIR spectra contain overtone and combinations features, which would require extensive (off-line) processing to deconvolute. This makes assessment of the sensitivity of this technique to blend change more difficult; peak height measurement can be misleading, but has been used for an indication of the apparent sensitivity. Analysis for the 10 wt% steps in blend concentration, using partial least squares regression analysis of the predicted

concentration of each polymer, gave a standard deviation of prediction of ± 0.39 wt%.

3.4. In-line Raman

Changes in the intensity of the peaks relating to specific vibrational modes within each polymer component were observed during extrusion $3010\text{--}200\text{ cm}^{-1}$. In general, Raman measurements involve a large fluorescent background related to additives, impurities, turbidity, temperature and pressure effects. There is also no internal standard for calibration. A time series plot of the Raman spectra accumulated at 785 nm every minute during blend extrusion for the region $1600\text{--}200\text{ cm}^{-1}$,

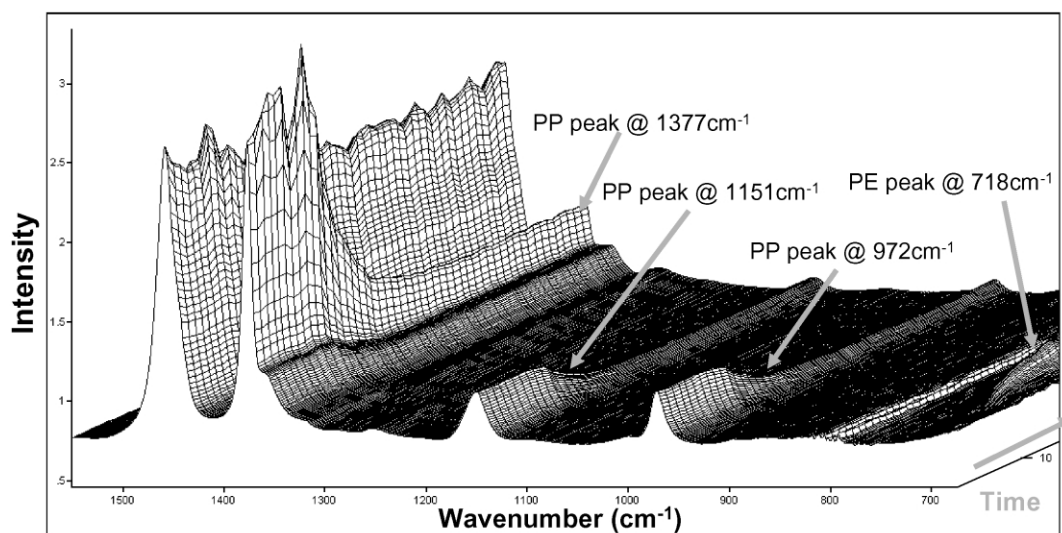


Fig. 6. 3D plot of on-line MIR spectra showing changes in peak intensity during extrusion of the PP:PE blends.

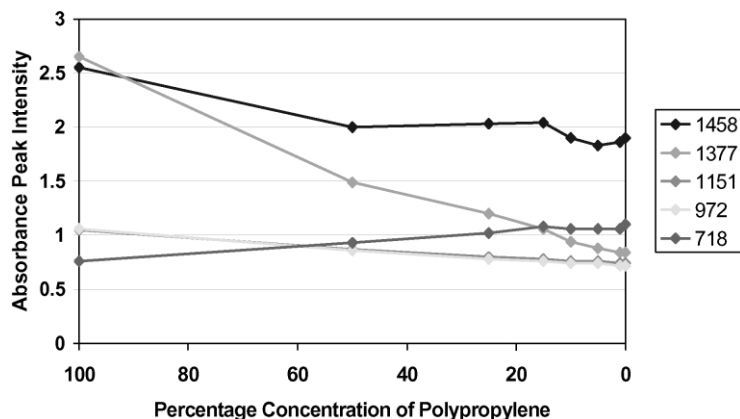


Fig. 7. On-line MIR peak intensity versus wt% of PP for chosen spectral peaks at 1458, 1377, 1151, 972 and 718 cm^{-1} .

where most change with blend concentration was observed, is presented in Fig. 10. This wavenumber range has been used in multivariate analysis, and the two most isolated peaks were monitored for calibration (univariate analysis). A peak unique to PP at 810 nm (400 cm^{-1} shift) was observed to increase in intensity, along with a decrease in the intensity of a PE peak at 858 nm (1080 cm^{-1} shift) during extrusion of the blends. The relationship between the intensity of each peak with blend concentration is shown in Fig. 11. The scattering intensity of each peak has a linear relationship to the change in concentration of the respective polymers. Partial least squares regression analysis of the predicted concentration of each polymer gave a standard deviation of prediction of $\pm 0.95 \text{ wt\%}$, reflecting the somewhat noisier spectra and fluorescent emission (evidenced by the baseline changes in Fig. 11) in these experiments, compared with in-line transmission NIR.

3.5. Ultrasound

Stepped material variation with time, from PE to PP, results in an increasing transit time, shown in Fig. 12. This is

linked to changes in bulk modulus and density [34] with blend ratio. As expected, a linear relationship is observed between transit time change and wt% polyethylene for the pertaining actual conditions of melt temperature and pressure, for the chosen extruder set temperatures and a screw speed of 15 rpm. This can be seen in Fig. 13 for two sets of experimental data, for the 10 wt% blend step tests. The apparent sensitivity of this measurement, namely the gradient of $\sim 24 \text{ ns/wt\%}$ (not corrected for any effects of melt pressure change), indicates that the ultrasound technique, with better than 1 ns resolution used here, should readily detect a 1 wt% change in blend. In fact, a 1 wt% PP:99 wt% PE blend in a different experimental run was readily detected using ultrasound transit time, but was not detected using on-line process spectroscopy under normal in-process conditions described earlier.

The peak height of the first transmitted signal was observed to drop as percentage of PP increased. Attenuation within the melt alone, however, (calculated from the first and second received echoes) was observed to decrease slightly as the proportion of PP increased.

Although melt temperature is maintained at a relatively steady value according to infrared temperature measurements,

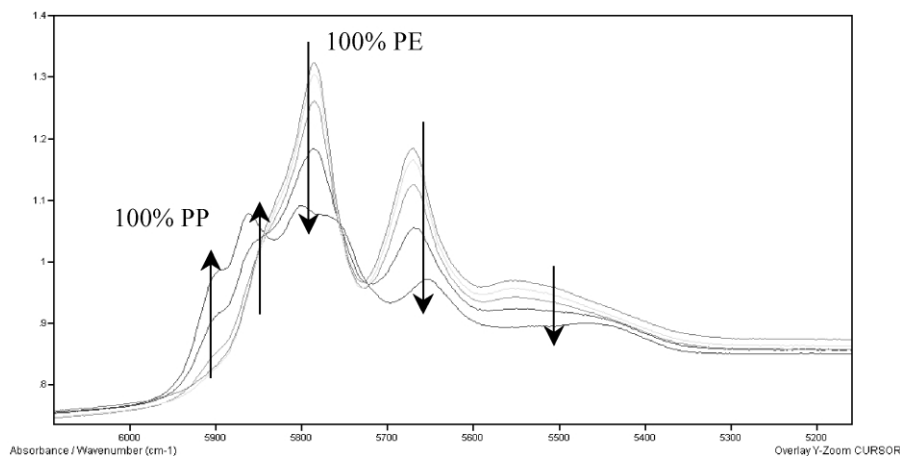


Fig. 8. On-line NIR spectroscopy: spectral changes with material change from 100 wt% polyethylene to 100 wt% polypropylene. Upward arrows indicate features which increase with increasing wt% PP, and downward arrows indicate features which decrease with decreasing wt% PE.

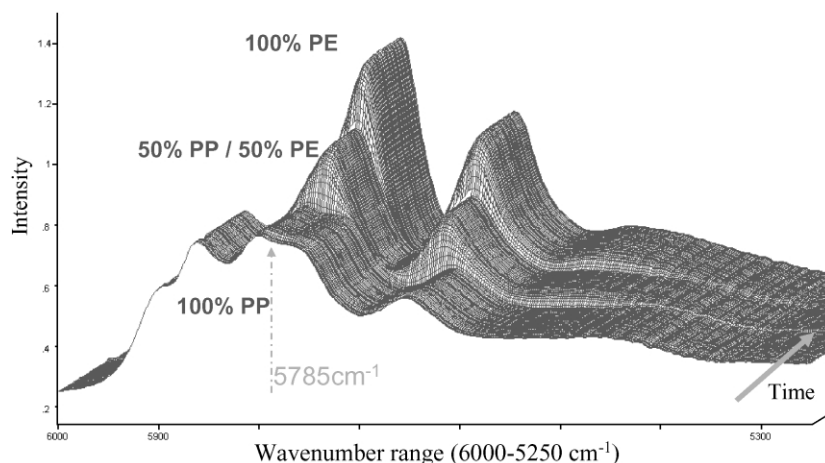


Fig. 9. In-line Raman spectra ($1600\text{--}100\text{ cm}^{-1}$) taken every minute during sequential extrusion 100% PE–100% PP, 15 rpm, $200\text{ }^{\circ}\text{C}$.

melt pressure in the die did vary, decreasing with the percentage of PP present. As previously noted [21], melt pressure is itself an indicator of change in melt state (through shear viscosity changes, as is the case here with change in blend ratio) but melt pressure measurements do not have the sensitivity observed for ultrasonic velocity variation, in particular in the PP-rich blends.

4. Comparison of the techniques

A comparison between changes in ultrasonic transit time and mid-infrared peak intensity for selected changeovers of HDPE/PP blends is shown in Fig. 14 for the change from 100% PP to 25 wt% PP:75 wt% PE, using the most sensitive spectral feature from the mid-infrared measurements, at 1377 cm^{-1} . Data are time shifted (to account for the measured 7 min time delay between the two processes). The

observed change in the blend composition obtained from the two techniques are in good agreement. These measurements give an indication of the dynamics of the changeover of feed material in the extruder (and can be used in building control models).

Changes in the ultrasonic transit time and Raman peak intensity for each of the PE/PP blends were also compared. Fig. 15 shows an initial comparison of the two techniques to monitor extrusion of 100% PP–100% PE via a 50/50 blend. The data demonstrate close agreement of the two methods. Further studies are in progress.

Under our experimental conditions, it was found that the ultrasound technique could successfully resolve a change of 1 wt% PP in HDPE, whereas the infrared spectroscopy exhibiting the best resolution in these experiments, the in-line NIR, could not resolve better than $\sim 2\text{ wt}\%$.

In general, MIR spectroscopy would normally be preferred for sensitivity and analysis in assessing change

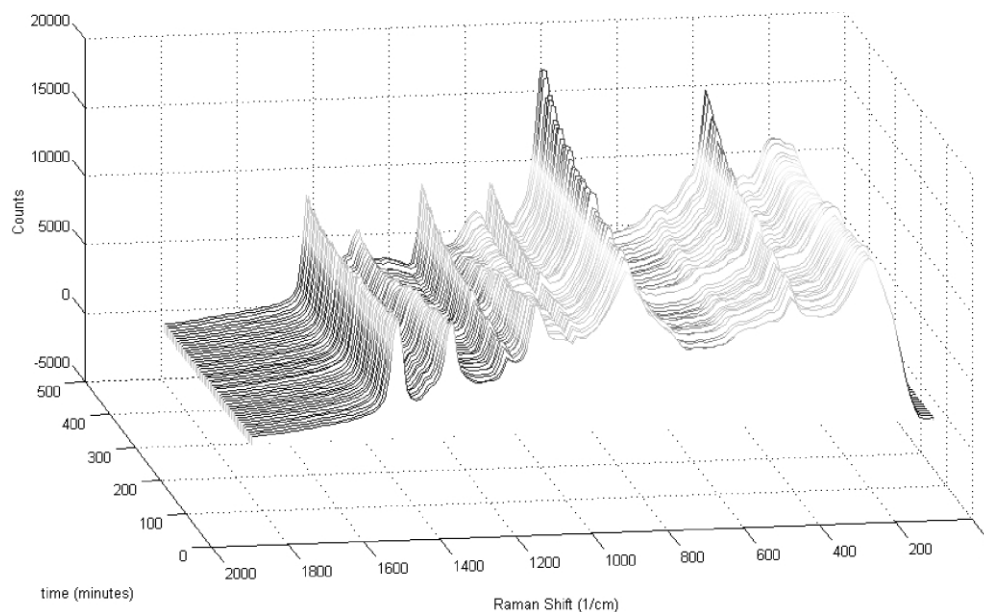


Fig. 10. 3D plot of Raman spectra taken every minute during sequential blend extrusion ($1600\text{--}100\text{ cm}^{-1}$) 100% PE–100% PP, 15 rpm, $200\text{ }^{\circ}\text{C}$.

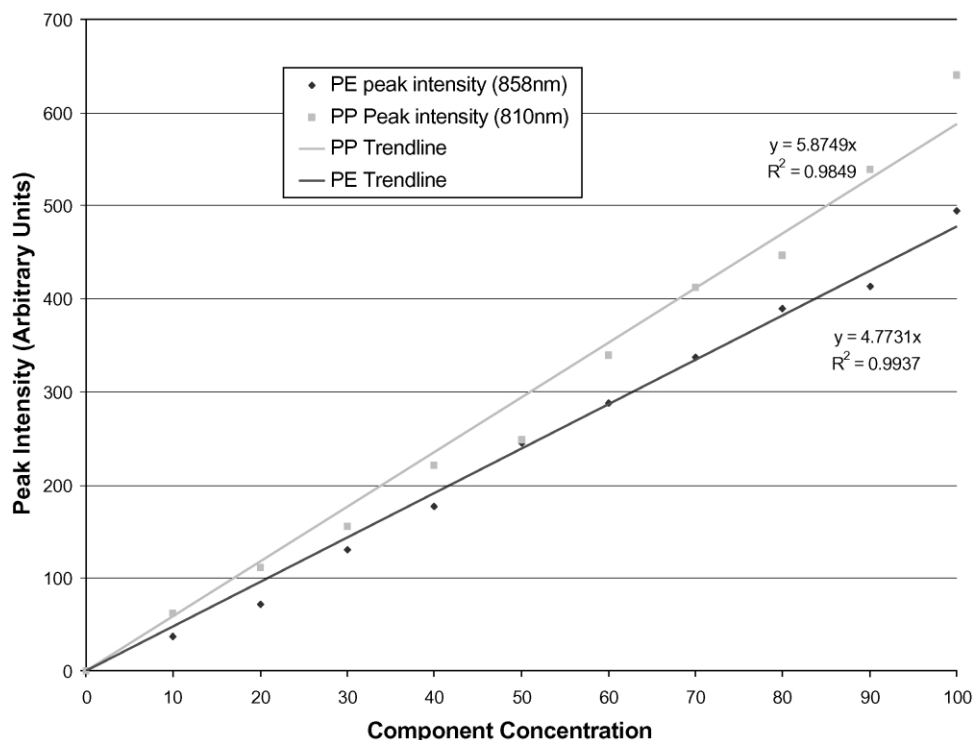


Fig. 11. In-line Raman spectroscopy—change in intensity of selected PP and PE peaks with change in the respective concentrations of PP or PE.

in a process, since fundamental vibrations are observed. However, this technique requires very small melt path lengths (~ 0.01 mm) which would not normally be practical for most melt processing operations. MIR would normally be expected to be used in on-line mode only—with consequent time delays, and issues concerning the on-line stream being discarded or returned to the main flow. NIR signals are typically an order of magnitude smaller than for MIR for the same melt path lengths, but by using melt path lengths which are more acceptable for in-line transmission process

measurements, namely ~ 1 – ~ 10 mm, very acceptable signals are obtained. The problem remains, however, that overtones and combination bands are being measured, making it difficult to quantify in real time changes in specific bond vibrations. Even so, in-line NIR spectroscopy is of significant interest for real time process monitoring. In-line Raman scattering has also shown much promise, offering good sensitivity.

Ultrasound is currently the most sensitive indicator of change in the blends observed here—but clearly suffers from the drawback that it can currently only indicate

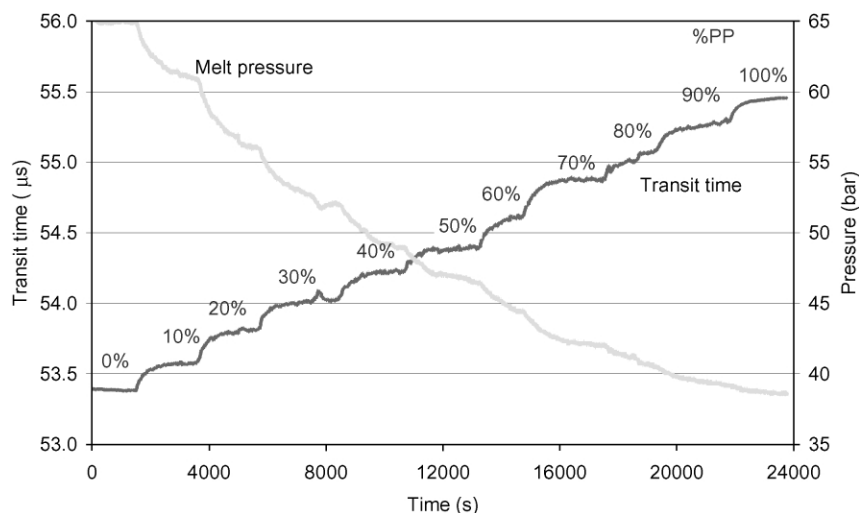


Fig. 12. Change in ultrasonic transit time and melt pressure during sequential extrusion of blends.

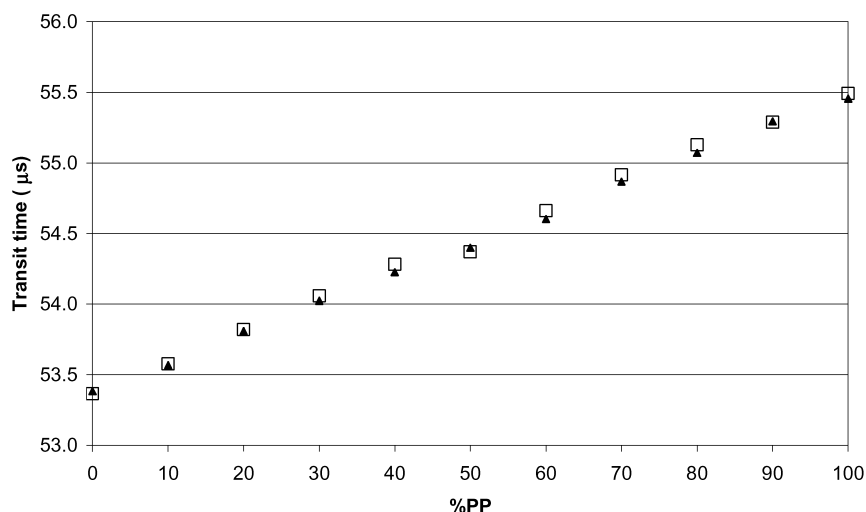


Fig. 13. Change in ultrasonic transit time with percentage PP, comparing two sets of experimental data.

change, but cannot give the level of molecular specificity which vibrational spectroscopy offers.

5. Conclusions

- In-process Infrared and Raman have been shown to give good quality spectra for polymer melts in the extrusion process, at data capture rates which are useful for process monitoring, and which provide specific information relating to bonds present within a polymer, providing detail of material type in the melt stream. Resolution was found to be limited in the reported studies, and an HDPE:PP blend ratio change of 1 wt% could not be resolved. Of the vibrational techniques explored, in-line NIR provided the most accurate assessment of blend ratio change, for the experimental conditions.

- Ultrasonic velocity measurements in through transmission mode provide a rapid assessment of bulk properties across the melt stream, demonstrating to the operator that a change has occurred, but not the cause of the change. Ultrasonic measurements respond quickly and are highly sensitive to change in PE/PP ratio.
- The spectroscopic and ultrasonic techniques provide excellent agreement regarding the transient changes of material, such as would occur in material changeover in extrusion.
- Near real time in-process vibrational spectroscopy techniques—on-line MIR, on-line NIR, in-line NIR and in-line Raman—have consequently been shown to be feasible. Technology (sensor, fibre optics, detector) and software developments (increasingly powerful chemometrics) will ensure actual real time analysis can be achieved.

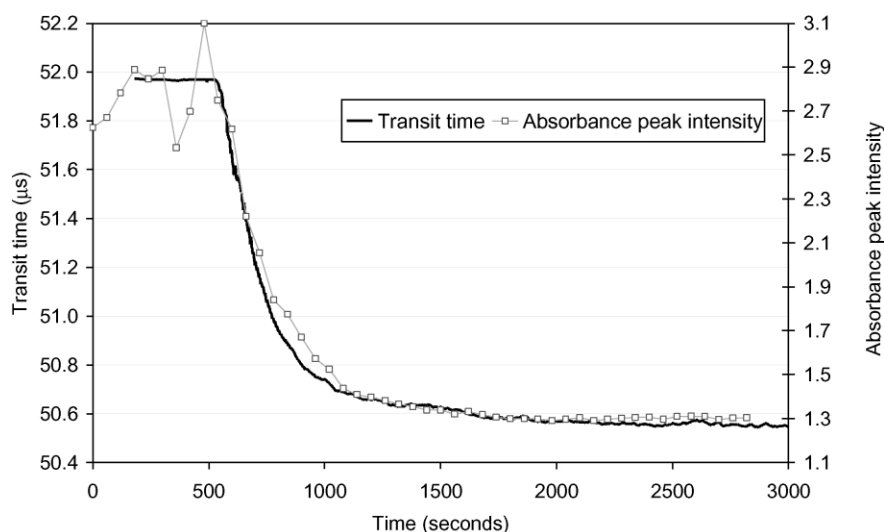


Fig. 14. Comparison of response time characteristics of ultrasonic transit time and mid infrared absorbance peak intensity during extrusion of 100% PP followed by 25 wt% PP/75 wt% PE blend.

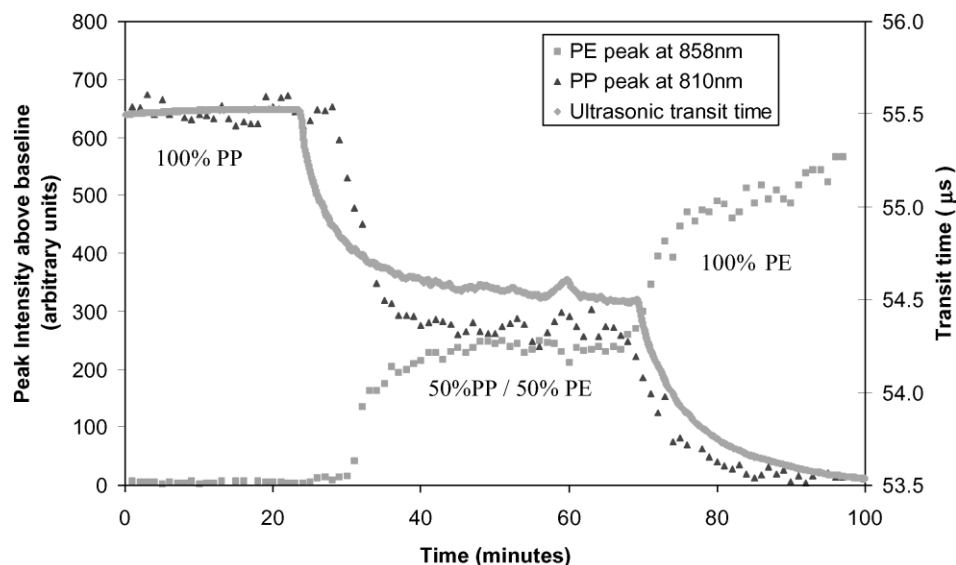


Fig. 15. Comparison of Raman peak intensity with ultrasonic transit time during extrusion from PP to PE via a 50/50 blend.

Acknowledgements

The authors are grateful for support of the EPSRC, the DTI MPM1.4 programme, and the IRC in Polymer Science and Technology.

References

- [1] Coates PD. Polymer processing: in-process measurements. Encyclopedia of materials; science and technology, New York: Pergamon Press; 2001. Chapter 46.
- [2] Coates PD, Kelly AL, Rose RM, Woodhead M. In-process shear flow measurements in extrusion and injection moulding. Bradford University; 1998. ISBN 1 85143 171 3.
- [3] Coates PD, Kelly AL, Rose RM, Woodhead M. In-process entry pressure measurements in extrusion and injection moulding. Bradford University; 1998. ISBN 1 85143 173 X.
- [4] Coates PD, Kelly AL, Martyn MT, Rose RM, Woodhead M. In-process extensional flow measurements in extrusion and injection moulding. Bradford University; 1999. ISBN 1 85143 174 8.
- [5] Kelly AL, Woodhead M, Rose RM, Coates PD. In process monitoring of polymer batch to batch variation in injection moulding. *Plast Rubb Compos* 2000;29(1):23–30.
- [6] Speight RG, Coates PD, Hull JB, Peters C. In-line process monitoring for injection moulding control. *Proc I Mech E Part E* 1997;211: 115–28.
- [7] Kelly AL, Coates PD, Dobbie TW, Fleming DJ. On-line rheometry: shear and extensional flows. *Plast Rubb Compos Process Appl* 1997; 25(7):313–8.
- [8] Martyn MT, Nakason C, Coates PD. Measurement of apparent extensional viscosities of polyolefin melts from real process contraction flows. *J Non-Newtonian Fluid Mech* 2000;92:203–26.
- [9] Khettry A, Hansen MG. *Polym Engng Sci* 1996;36:1232.
- [10] Hansen MG, Vedula S. In-line measurement of copolymer composition and melt index. In: Coates PD, editor. *Polymer process engineering 97*. London: Institute of Materials; 1997. p. 89–102. ISBN 1-86125-044-4.
- [11] Herman H, Hope PS. Illuminating the manufacturing process—on-line UV spectroscopic analysis. In: Coates PD, editor. *Polymer process engineering 97*. London: Institute of Materials; 1997. p. 65–77. ISBN 1-86125-044-4.
- [12] Rauwendaal CJ, Fernandez F. Experimental study and analysis of a slit die viscometer. *Polym Engng Sci* 1985;25(11):765–71.
- [13] Pabedinskas A, Cluett WR, Balke S. Development of an in-line rheometer suitable for reactive extrusion process. *Polym Engng Sci* 1991;31(5):305–75.
- [14] Coates PD, Rose RM, Woodhead M, Kelly AL. Sensitivity of in-line rheometry for extrusion of $Mg(OH)_2$ filled LDPE compounds. *Int Polym Process* 1998;XIII(2):172–82.
- [15] Purvis J, Bower DI, Ward IM. *Polymer* 1973;14:398–400.
- [16] Jarvis DA, Jutchinson II, Bower DI, Ward IM. *Polymer* 1980;21: 41–54.
- [17] Lapersonne P, Bower DI, Ward IM. *Polymer* 1992;33:1266–76.
- [18] Cole KC, Ajji A. In: Edward IM, Coates PD, Dumoulin M, editors. *Solid phase processing of polymers*. Munich: Carl Hanser; 2000. chapter 3, ISBN 1-56990-307-7.
- [19] Siesler HW, Holland-Moritz K. *Infrared and Raman spectroscopy of polymers practical spectroscopy*, vol. 4. New York: Marcel Dekker; 1980.
- [20] Fischer D, Bayer T, Eichhorn KJ, Otto M, Fresenius. *J. Anal. Chem.* 1997;359:74–7.
- [21] Sibley MG, Brown EC, Edwards HGM, Coates PD. Combined IR spectroscopy and ultrasound studies of changing melt composition during single screw extrusion. *SPE Tech Pap* 2001;XLVII:3100–4.
- [22] Wilson RH, Tapp HS. *Trends Anal Chem* 1999;18(2):85.
- [23] Chung H, Ku M-S, Lee J-S. *Vibrational spectroscopy* 1999;20:155.
- [24] Schmitt J, Flemming H-C. *International biodeterioration and biodegradation* 1998;41:1.
- [25] Blanco M, Coello J, Iturriaga H, Maspocho S, Pagès J. *Anal Chim Acta* 1999;383:291.
- [26] van Uum MPB, Lammers H, de Kleijn JP. *Macromol Chem Phys* 1995;196:2023.
- [27] Dhamdhare M, Li J, Deshpande B, Patil P, Hansen MG. At-process Raman spectrometry of polymer melts. In: Coates PD, editor. *Polymer process engineering 01*. London: IoM Communications Ltd; 2001. p. 46–58. ISBN 1-86125-148-3.
- [28] Piche L. Ultrasonic probe for on-line process monitoring. *SPE Tech Pap* 1998;44:3617.
- [29] Brown EC, Olley P, Coates PD. In-line melt temperature measurement during real time ultrasound monitoring of single screw extrusion. *Plast Rubb Compos* 2000;29(1):3–13.

- [30] Brown JM. Molecular spectroscopy. Oxford, UK: Oxford University Press; 1998.
- [31] Overall N, King B. Raman spectroscopy for characterisation in an industrial environment. *Macromol Symp* 1999;141:103–16.
- [32] Edwards HGM, Garcia-Pichel F, Newton EM, Wynn-Williams DD. Vibrational Raman spectroscopic study of scytonemin, the UV-protective cyanobacterial pigment. *Spectrochim Acta Part A* 2000;56:193.
- [33] McSkimin HJ. In: Mason WP, editor. *Physical acoustics, principles and methods*, vol. 1. New York: Academic Press; 1964. part A, Chapter 4.
- [34] Brown EC. Ultrasonic monitoring of polymer melt extrusion. PhD Thesis, University of Bradford, UK; 1998.
- [35] Brown EC, Collins TLD, Dawson AJ, Olley P, Coates PD. Ultrasound: a virtual instrument approach for monitoring of polymer melt variables. *J Reinf Plast Compos* 1999;18:331–8.
- [36] Smith G, Brown EC, Coates PD. Sensitivity of ultrasonic velocity and attenuation measurements to temperature, pressure and filler concentration for magnesium hydroxide filled LDPE and HDPE. *SPE Tech Pap* 2001;XLVII:3105–9.