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Raman Spectroscopy for Polymer Characterization in an Industrial Environment

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SUMMARY: In this paper we discuss the use of Raman spectroscopy for characterising polymers both in the laboratory and also in-situ at the production line. We show how polymer crystallinity can be followed during extrusion and drawing, and describe the compositional analysis of cross-linked acrylic terpolymers in a polymerisation reactor. We also discuss problems which can arise such as sample fluorescence from moving polymers, distortion of relative band intensities due to chromatic aberration, and sampling difficulties with turbid solutions.

Introduction

Raman spectroscopy makes an important contribution to the measurement of polymer composition and microstructure. Here we use the example of a styrene - acrylic terpolymer to show how Raman band intensity measurements and multivariate calibration techniques can be used to measure composition. We will also discuss measurement of polymer composition and morphology on-line using a process Raman analyser, and highlight some of the benefits and pitfalls associated with Raman spectroscopy as an on-line technique.

Band intensity ratios for measuring acrylic terpolymer composition

Raman spectroscopy is a quantitative technique since, to a first approximation, the intensity of a band is linearly proportional to the concentration of the scattering units. However, it is not an *absolute* technique, i.e. the constant of proportionality between band intensity and concentration must be obtained by calibrating with samples of known composition. In addition, band intensities will depend upon many factors, including laser power, efficiency of collection optics, sample refractive index etc, so the absolute Raman band intensity is

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rarely useful for quantitative analysis. Instead, one usually normalises the intensity of the band of interest relative to that of an "internal standard" such as a solvent peak, or a band due to another constituent of the polymer.

The system we use to illustrate compositional measurements is a terpolymer of methyl methacrylate (MMA), butyl acrylate (BuA), styrene, and a di-unsaturated cross-linker. Measuring and optimising composition is important to control the optical and mechanical properties of the particles. Because the commercial rubber is cross-linked and insoluble, solution-state NMR spectroscopy cannot be used to confirm the composition either of our own materials or competitive products. However, one can produce rubbers with a range of compositions but *without* cross-linker, analyse them using NMR, and then use these samples to calibrate the Raman spectra in terms of styrene, MMA and BuA level. Raman spectroscopy can then be used to analyse fully formulated, cross-linked materials, on the assumption that a low level of cross-linker does not perturb the spectrum.

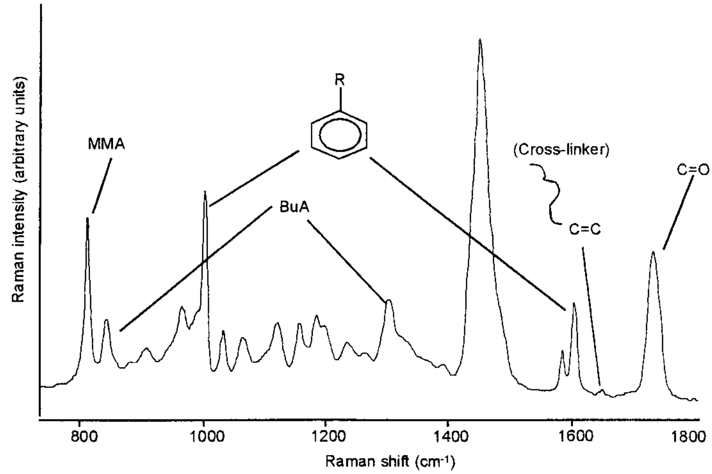

Figure 1. Major Raman band assignments for a partially crosslinked styrene/MMA/BuA copolymer

Figure 1 illustrates the Raman spectrum of a typical rubber sample. Bands are highlighted which correlate with MMA, BuA and styrene level. In addition, a C=C band from residual incompletely-reacted cross-linker can be seen – we find that the polymer has pendant side chains due to cross-linker which has reacted only at one end. Calibration for overall composition is achieved in two steps. First, we define I_1/I_2 as the peak height ratio of the styrene ring mode at 1603 cm^{-1} relative to the ester carbonyl stretch (1731 cm^{-1}), and M_S, M_{MMA} and M_{BuA} as the masses of each component. Plotting I_1/I_2 versus $M_S/(M_{MMA} + M_{BuA})$ yields an excellent linear calibration (Fig.2a) which allows the styrene/(total acrylic) mass ratio of a rubber to be determined. Surprisingly, the relative intensity of the C=O band depends only on the *combined* mass of MMA and BuA, rather than also on the *relative* levels of MMA and BuA in the acrylic component. This is purely fortuitous-it indicates that the difference in molecular mass between the MMA and BuA is compensated by the difference in intrinsic Raman scattering efficiency.

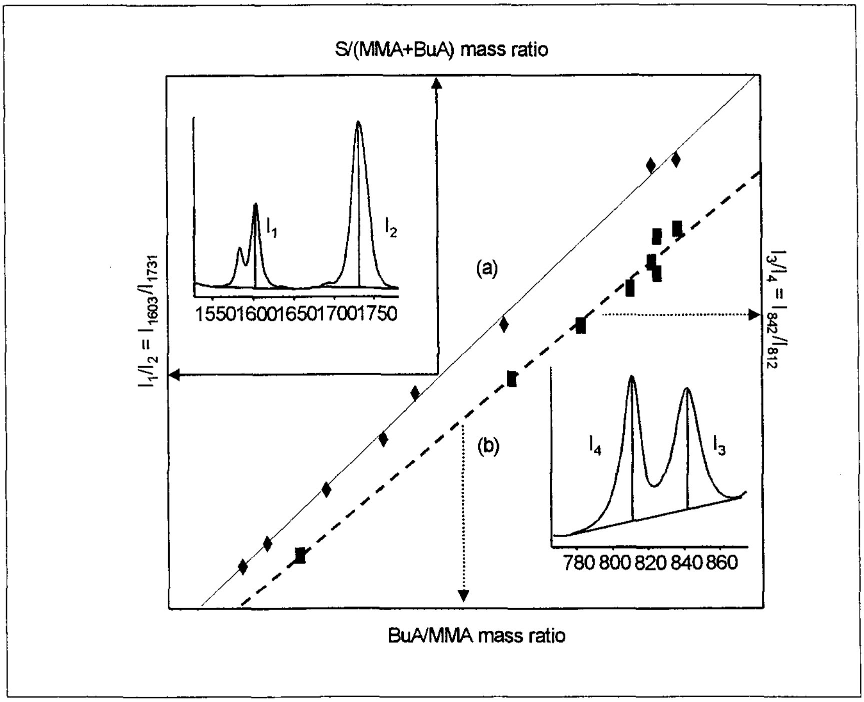

Figure 2. Calibration for composition of styrene/BuA/MMA terpolymer using band intensity ratios. Line (a) gives the ratio styrene/(BuA+MMA), line (b) gives the BuA/MMA mass ratio

Figure 2b shows a similar calibration for the BuA/MMA mass ratio (Fig. 2b). Here I_3 is the intensity of a band near 842 cm^{-1} and I_4 the intensity of the band near 812 cm^{-1} which correlate with BuA and MMA content respectively. Again, a good calibration was obtained. Knowing the styrene/acrylic mass ratio and the MMA/BuA mass ratio we can determine the total composition of an unknown material.

This analytical method is valuable because it allows an otherwise intractable sample to be characterised, and in this case it also shows that not all of the cross-linker has reacted in the final product, contrary to expectations. (By incorporating known amounts of unreacted cross linker in the calibration set, an estimate for residual cross-linker could be obtained if desired). Obviously, this approach can be applied, in principle, to any copolymer with an arbitrary number of components, provided that each component gives rise to a unique band. This approach has been used widely for copolymer analysis, for example high performance aromatic thermoplastics 1,2), a variety of rubbers 3), copolymers of dimethylbutadiene with methylmethacrylate 4), and elastomers 5). However, calibrations are unlikely to be linear over extreme ranges of copolymer composition, since the intrinsic band intensities and positions will depend upon the polymer sequence, which in turn may depend upon overall composition.

Multivariate calibration for polymer composition

Sometimes it is difficult to identify bands which correlate uniquely with individual components, or bands may be heavily overlapped, making it difficult to select appropriate features for the optimum calibration. In such cases, multivariate calibration techniques, in particular Partial Least Squares (PLS) modelling, can offer a powerful alternative. Here we illustrate the application of PLS calibration to the acrylic terpolymer data set described earlier.

Figure 3 shows the optimum calibration (predicted versus actual % mass), for each component, with the individual models combined into one plot for simplicity. In this model, all spectra were first pre-processed by normalising to unit area, as this has been shown to be effective in minimising variance induced by changes in laser power and sample alignment which would otherwise perturb the Raman intensities 6). All data were mean-centred and PLS models formed using the %S, %MMA and %BuA as the calibrant data. In each case a separate model was constructed for each component (PLS1). The optimum number of factors was determined by cross-validation with “leave one out” sample rotation, using the F statistic with a cut-off probability of 0.75 7). After refinement it was found that the best prediction for %S was obtained using a 2 factor model over the spectral range 760-1800 cm^{-1}, yielding a Standard Error of Calibration (SEC) of 0.2%. The best predictions for MMA and BuA (SEC's ~ 1%) were obtained using a 2-factor model over the region 2600-3300 cm^{-1}. This illustrates the need to optimise the calibration region *for each individual component.*

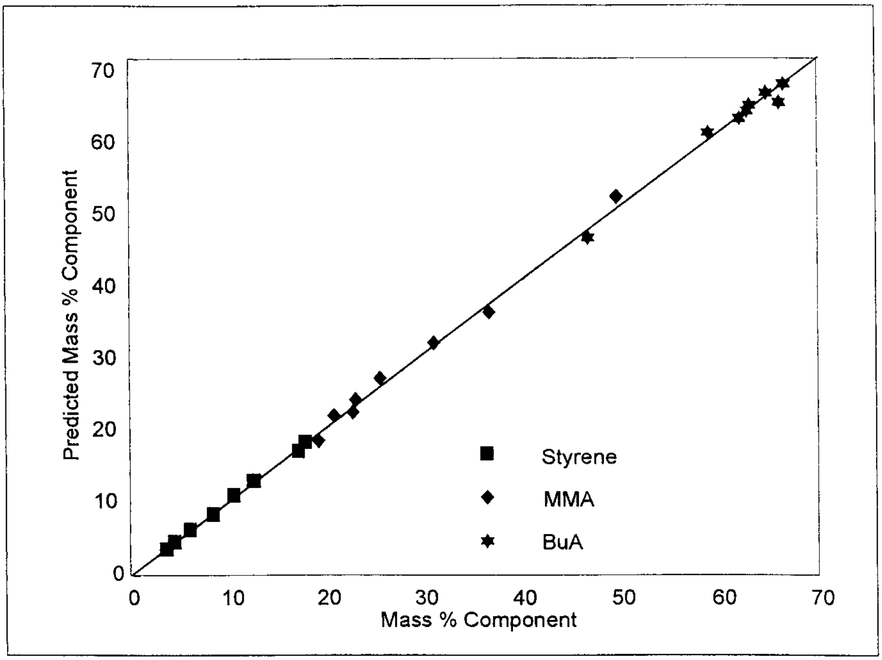

Figure 3. PLS calibration models for styrene/acrylic terpolymer composition. The optimum number of factors in each case was two. Redrawn from Figure 11 of ref.10)

It is important to examine the form of the factors to ensure that the model can be rationalised physically or chemically. For example, Figure 4 shows loadings plots for the two factors used for the styrene calibration, overlaid with a spectrum of atactic PS. In this case interpretation is straightforward - factor 1 is essentially the spectrum of PS, plus additional weak negative components due to PMMA and positive features from PBuA. Factor 2 has predominantly positive PMMA and negative PBuA features. This is a typical result - the factors resemble linear combinations of the spectra of individual components, and a linear combination of factors 1 and 2 will yield a spectrum similar to that of styrene.

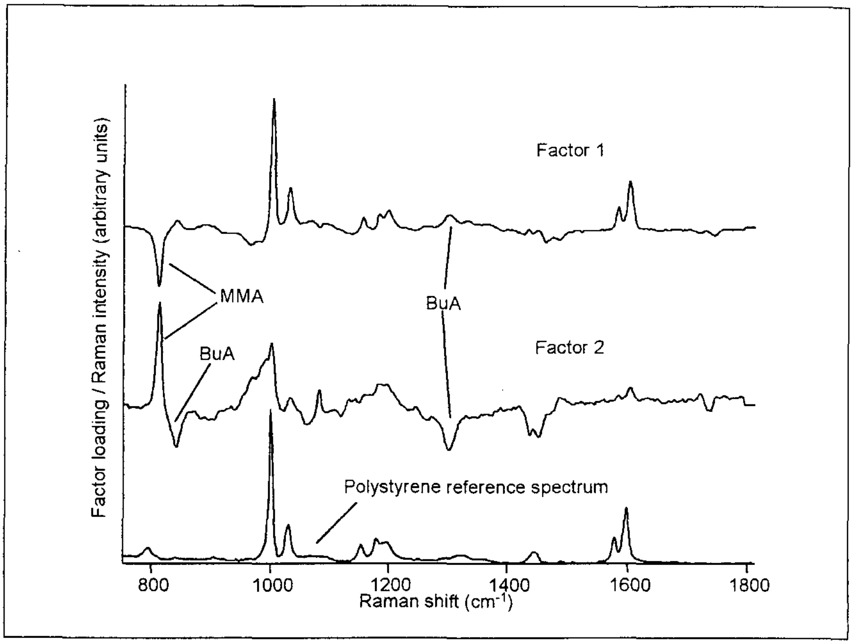

Figure 4. Loadings plot for styrene calibration. Redrawn from Figure 12 of ref.10)

Polymerisation kinetics and degree of polymerisation

Polymerisation often leads to perturbation of a strongly Raman-active group. In such cases the ease of obtaining Raman data through glass windows or the walls of reaction flasks make it an ideal technique for following polymerisation in-situ in the laboratory or the production environment. The limitations are solely in terms of ability to acquire good S/N data on the appropriate timescale, and the potential fluorescence of the reaction mixture.

Raman spectroscopy is very useful for monitoring polymerisation of unsaturated monomers such as acrylates and styrene 8). Interestingly, this work highlights an important aspect of choosing the internal standard – the absolute intensity of the "internal standard" band must be checked to ensure that it doesn't change during reaction, or the extent of any change must be measured. For example, in the case of styrene polymerisation, the intensity of the 1602 cm^{-1} ring mode was over *five times* higher for the monomer than for the polymer9), and this mode has been used as an internal standard. Failure to correct for this effect grossly distorts the calculated monomer consumption results, but provided we know the ratio of intrinsic scattering intensities for the standard band in monomer and polymer, correction is actually quite straightforward [10).

Although relatively little has been published on monitoring vinyl polymerisation under real production conditions, process Raman analysis is well suited to this application and is probably being widely used. For example, Leugers [11) reported the use of on-line Raman to monitor monomer conversion in the heterogeneous catalysis of the production of syndiotactic PS. We have used a fibre-coupled analyser to monitor batch production of the styrene/acrylic terpolymer described earlier. Data were obtained directly through the glass window of a reactor containing an aqueous emulsion of MMA, BuA, styrene, cross-linker, and polymer. Figure 5 shows time-resolved spectra of the latex in the reactor, which was being continuously fed by varying monomer streams.

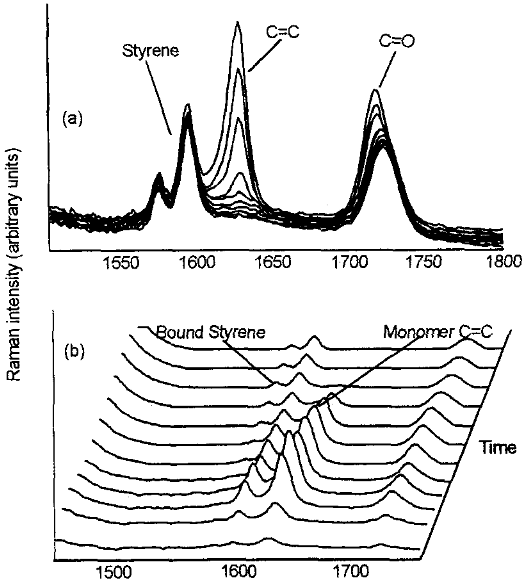

Figure 5. Changes in Raman spectrum of latex during polymerisation

Changes in composition, such as variation in (a) total C=C intensity and (b) incorporation of bound styrene are readily seen. Simultaneously differentiating and measuring the levels of free MMA, BuA, styrene, and their respective polymerised products, is far from trivial and is still under development, but some useful information can be obtained. Using techniques such as curve resolution/deconvolution and multivariate analysis, subtle differences in the C=C stretching frequency (as low as 1cm^{-1}) should allow quite similar comonomers to be distinguished in reacting media (12), with the possibility of quantifying the complete monomer mix.

On-line measurement of morphology/composition

The properties of a polymer product depend not just upon its degree of polymerisation but also on its crystallinity, orientation, and often the levels of additives, fillers and blended components. It is useful to be able to monitor these parameters non-invasively without perturbing the production line. Raman is ideal for obtaining spectra without contact from moving fibres, films, sheets etc. However, many solid polymers will be prone to the problem illustrated by Figure 6.

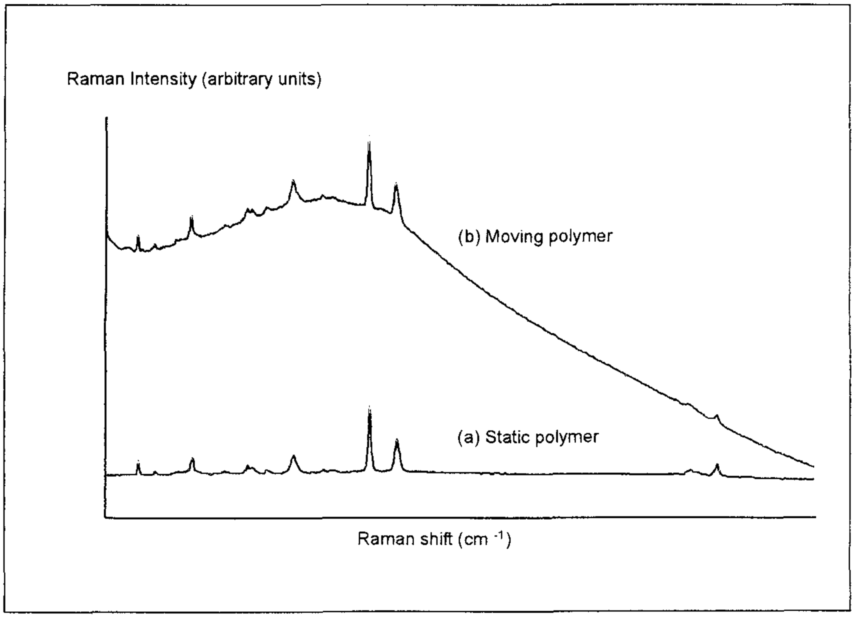

Figure 6. Failure of fluorescence quenching with moving polymers. Spectra obtained with 532 nm excitation. Redrawn from Figure 29 of ref. (10)

Spectrum (a) was obtained from an extruded, drawn polymer held static in the laser focus (532 nm excitation) - there was no discernible fluorescence. Spectrum (b) was obtained from exactly the same polymer with the production line running and polymer moving through the laser focus; clearly fluorescence was a significant problem! This effect is readily explained. Most samples, when initially placed in a visible laser beam, exhibit a burst of intense fluorescence which quickly diminishes. This "quenching" is due to bleaching or volatalisation of the fluorophores in the laser focus. However, on a production line fresh sample is continually moved through the laser focal volume and quenching is ineffective. Thus many samples which yield excellent static laboratory spectra can still fluoresce strongly when analysed under production conditions.

The obvious approach to minimise fluorescence is to use a longer wavelength laser for excitation. Figure 7(a) shows the spectrum of the same moving polymer, but this time using a 785 nm laser for excitation. Fluorescence was not excited even though the polymer is moving. Figure 7(b) shows the effect of introducing "reclaimed" or recycled polymer into the stream. Reclaimed material is often slightly degraded or contaminated, so even the deep red excitation causes some fluorescence in this case.

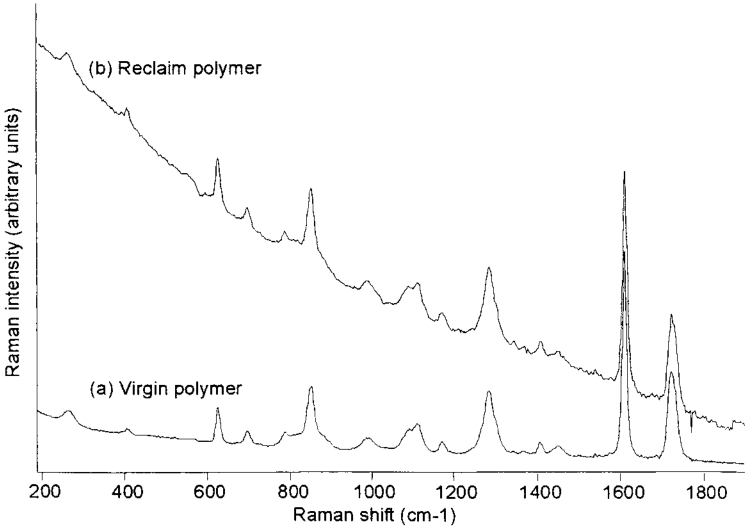

Figure 7 Raman spectra obtained from moving polymer under 785 nm excitation as a function of polymer purity. Redrawn from Figure 30 of reference [10)]

One might assume that the logical extension of this approach is to use 1064 nm excitation (e.g. FT Raman spectroscopy) to more effectively minimise fluorescence. The problem here is the trade off between minimising fluorescence and decreasing the Raman signal due to poorer scattering efficiency at longer wavelengths. Generally a visible/deep red dispersive Raman system is much more sensitive than a FT system using 1064 nm excitation [13]. Hence an on-line, fibre-coupled FT system may not always be a practical solution owing to inadequate S/N or impractical collection times.

Even if a fluorescence background is present, provided that spectral S/N is adequate one can still extract useful information from Raman spectra. Fig. 8 shows (a) Raman data recorded from a melt-extruded polymer which has been subjected to different draw ratios and (b) a 2 component blend where the composition was varied during extrusion.

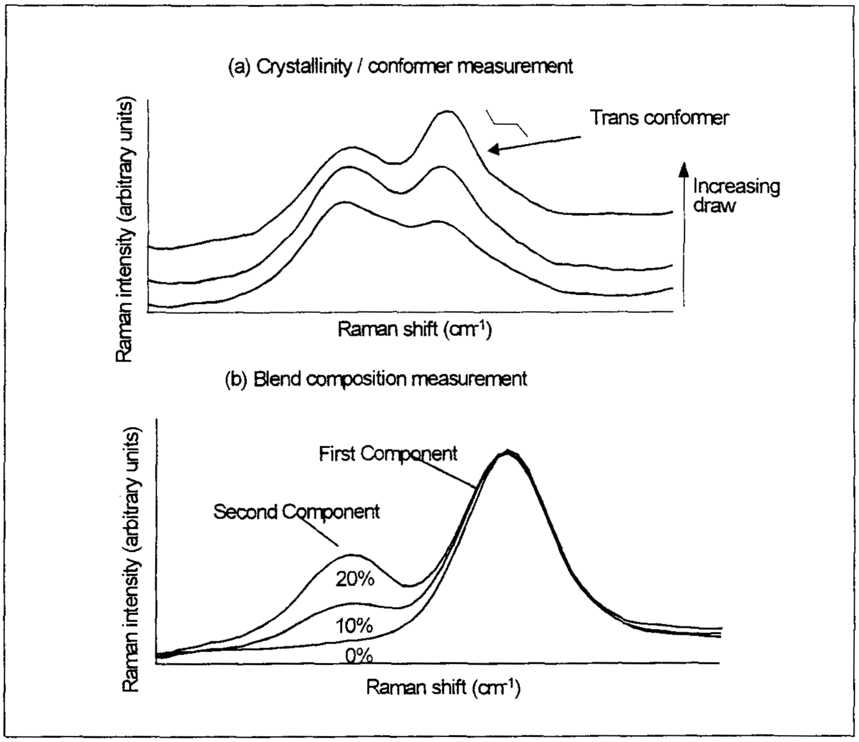

Figure 8 On-line Raman spectra obtained from extruded polymer, showing (a) changes in backbone conformation with increasing draw and (b) sensitivity to blend composition Redrawn from Figure 31 of reference [10]

Both sets of data were recorded from a polymer production line in real time under normal operating conditions, using a 532 nm laser. The laser was focused onto moving polymer immediately after it has been drawn up to four-fold relative extension. The spectra were baseline corrected to remove the fluorescence background. The S/N is adequate to show that (a) as the draw increases, a conformer present in the crystalline phase grows significantly, and (b) the blend composition can be monitored over the range of interest. This data was, we believe, the first example of polymer morphology and composition being measured on-line during production [14)] . It indicates the potential for monitoring and controlling polymer chemical and physical properties, during production, using a non-invasive probe to provide feedback for a control loop.

Difficult on-line sampling situations

Relatively little has been said so far about on-line sampling; partly this is because the engineering used to interface the spectrometer and production line is often critical and involves proprietary information. However, it is worth pointing out two specific, very important problems. Firstly, Figure 9 illustrates the problem of chromatic aberration, demonstrated in this case by translating a sample through the focus of a collection lens using 785 nm excitation.

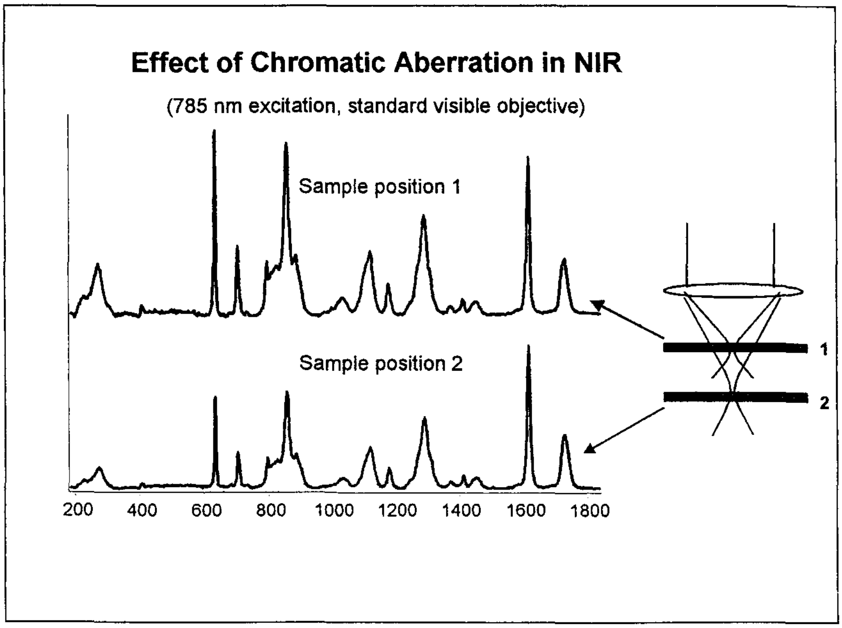

Figure 9. Effect of chromatic aberration on relative band intensities. The relative intensity of bands across the spectrum depends on the distance of the sample from the collection lens. The effect is greatest using NIR excitation, since corrections for chromatic aberration are more difficult in this wavelength range

If the collection lens is not well corrected, light of different wavelengths will be brought to a focus at different positions. *Moving the sample changes the relative intensity of bands throughout the spectrum because the optimum focus for a Raman band will depend upon its absolute wavelength.* Thus, unless one always places the sample at the same distance from the lens, subtle relative intensity changes can occur which will play havoc with multivariate data analyses. This effect does not appear to have been widely acknowledged, but is potentially very important, particularly when using NIR excitation. It can be minimised by using well-corrected lenses (ideally all-reflective).

Secondly, difficulties arise when turbid or highly absorbing liquids are studied since the laser beam cannot penetrate effectively into the sample. Figure 10 shows a dilute, turbid emulsion being analysed through a silica window. On adjusting the focus of the laser beam/collection optic, three distinct outcomes arise.

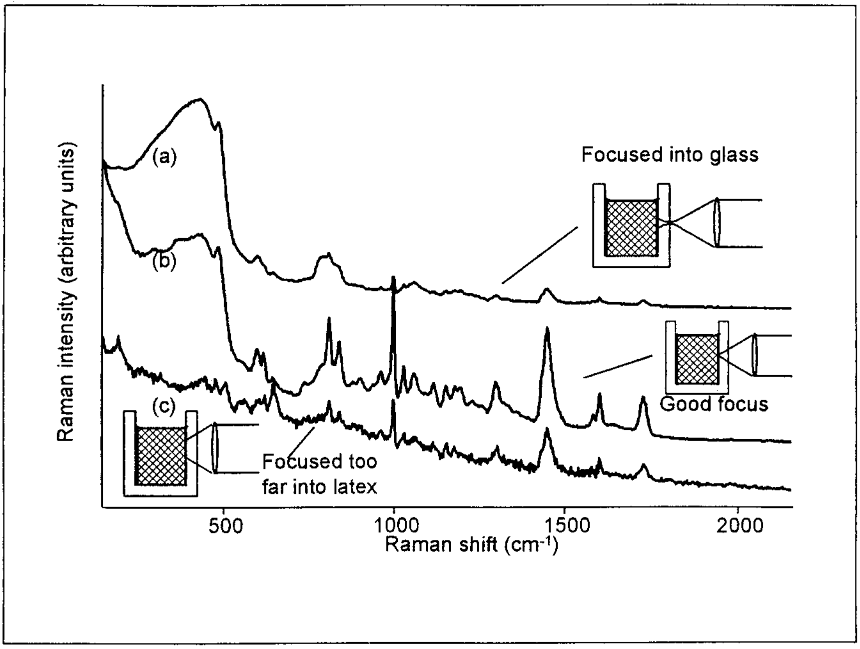

Figure 10. Effect of laser focus position with highly turbid or absorbing media. See text for details

If the laser is focused too far into the silica window (a), a strong silica background is obtained which can mask low frequency bands. If the laser is focused just at the interface of the liquid and the window, a relatively good spectrum is obtained, albeit with a weak silica background (b). If the laser is focused too far into the sample, it does not penetrate and a diffuse, out of focus spot is formed at the window/sample interface, resulting in a very poor spectrum (c). Only situation (b) is acceptable but this can be difficult to achieve if the optical properties of the solution change, for example during a reaction. This is difficult to tackle; an intelligent autofocusing system is one solution, but another option is to choose a window material which does not interfere with the Raman bands of interest. Useful alternatives include sapphire, quartz and diamond. These are discussed in more detail elsewhere [10)] Another important issue, which is too involved for discussion here, is the problem of window fouling. Considerable effort has been expended in designing window arrangements to minimise fouling or allow easy cleaning during use.

Conclusions

In the paper we have attempted to illustrate the versatility of Raman spectroscopy for on-line analysis of polymers. Using this technique one can readily analyse chemical composition and sample morphology during production, with the added advantage that the spectral variations and multivariate models can be interpreted and rationalised in terms of chemical or physical changes. This is a key benefit compared with NIR spectroscopy, where one usually relies upon a model which is difficult to interpret in physical, chemical or spectroscopic terms.

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References

[1]Hendra, P., Jones, C. and Warnes, G., "*Fourier Transform Raman Spectroscopy*", Ellis Horwood, New York 1991 pp.175-203
[2]Ellis, G., Sanchez, A., Hendra, P.J., Willis, H.A., Chalmers, J.M., Eaves, J.G., Gaskin, W.F. and Kruger, K., *J. Mol. Struct.* **247**, 385-95 (1991)
[3] Kurosaki, K., "*International Polymer Science and Technology*" **15**, T29-T38 (1988)

[4] Edwards, H.G.M., Johnson A.F., Lewis I.R., Ward N.J. and Wheelwright S., *J. Raman Spectrosc.* **24,** 495 (1993)

[5] Jackson K.D.O., Loadman M.J.R., Jones C.H. and Ellis, G., *Spectrochim. Acta* **46A,** 217 (1990).

[6] Everall, N, Tayler, P., Chalmers, J.M., Mackerron, D., Ferwerda, R. and van der Maas, J.H., *Polymer* **35**, 3184 (1994)

[7] Haaland, D.M. and Thomas, E.V., *Anal. Chem.* **60**, 1193 (1988)

[8] Gulari, E., McKeigue, K. and Ng, K.Y.S., *Macromolecules* **17**, 1822 (1984)

[9] Wang, C., Vickers, T.J., Schlenoff, J.B. and Mann, C.K.,, *Appl. Spectrosc.* **46**, 1729 (1992).

[10] Everall, N. in *"Raman spectroscopy of synthetic polymers"* in *"Analytical Raman Spectroscopy"* (ed. M. Pelletier), Blackwell, *in press.*

[11] Leugers, A., Arriola, D., Beaudoin, D. and Weston, J., Paper 670 in " *Abstracts of 24th FACSS conference, October 26-30th, Rhode Island";* 1997, p. 228

[12] Bowley, H.J., Gerrard, D.L., Smith, M.J.C. and Biggin, I.S., *Adv. Coat. Sci. Technol. Ser.* **11**, 1 (1989).

[13] Everall, N.J., Owen, H. and Slater, J., *Appl. Spectrosc.* **49**, 610 (1995)

[14] Everall, N.J. in *"An Introduction to Laser Spectroscopy"*, (eds D.L. Andrews and A.A. Demidov,) Plenum Press, New York, pp. 115-131(1995)