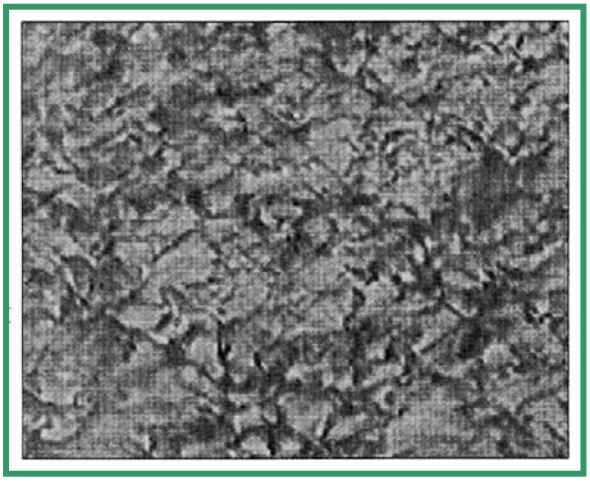
Localisation of Polymeric Phases by Raman Microscopy Mapping Components of a Blend in a Plane, and Depth Profiles of a Laminated Film

Use of polymers in new applications involves matching the materials properties with the applications requirements. Often a polymer will be engineered for the application. This involves selection of the monomers and designing the manufacturing processes in order to tailor mechanical properties such as toughness, hardness and elasticity, electrical properties (such as the ability to insulate or conduct), and optical properties. When more than one type of polymer is used in order to take advantage of the properties of the two (or more) chemical types, synergism can be achieved in the combination. The physical properties of the finished materials will depend on the chemical composition as well as the polymer's morphology (orientation, cristallinity and chemical dispersion). The chemical phases can be combined by two methods. If the material is co-polymerised, the monomers are controlled during the polymerisation process. In this manner separately polymerising N units of the 1st monomer, M units of the 2nd monomer, and then joining the blocks can make block co-polymers. Polymerising all monomers simultaneously will make random co-polymers. While co-polymerisation can provide a high degree of control of the final properties of the product, it is clearly an expensive manufacturing process. Blending, an alternative method for engineering products that combines the properties of polymer types is a physical mixing.

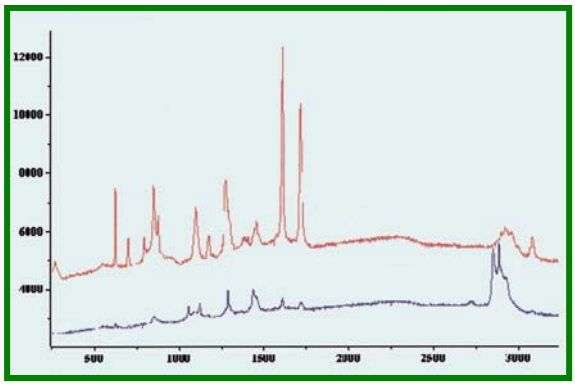
It has the advantage of being not only simple and inexpensive, but also allows for re-cycling used material. Incompatibility or non-miscibility of the differing chemical components is often an issue in the final performance of the polymer product. The first part of this note concerns the dispersion of the two components in a polyethylene-polybutylene terephthalate blend. The chemical imaging capabilities of the LabRAM will be used to get this information. The second part deals with the depth analysis of laminated films made of different polymer layers. Again, the chemical structure and thickness of the layers will influence the multilayer structure properties.

The dependence of the results on the confocal conditions will also be investigated.
Indeed, a good Z discrimination is necessary to achieve highly resolved depth profiles.



Phase Identification

This TV image of a 0.5 µm thick sample of the PE/PBT film illuminated in transmission indicates heterogeneities. The image shows contrast, but it was only when the Raman spectra were recorded that it became possible to say that the more transparent material contained PBT while the more opaque material contained higher concentrations of PE. Using the microprobing capability of the LabRAM, the two phases can be fingerprinted within seconds. The upper spectrum was recorded from the clear phase, and the lower spectrum was recorded from the darker material. By searching a polymer data base, it was possible to identify the clear material as PBT. The spectrum of the darker material had some residual bands from PBT, but most of the intensity was attributed to PE.



Polyethylene (PE) Polybutylene terephthalate (PBT) blend

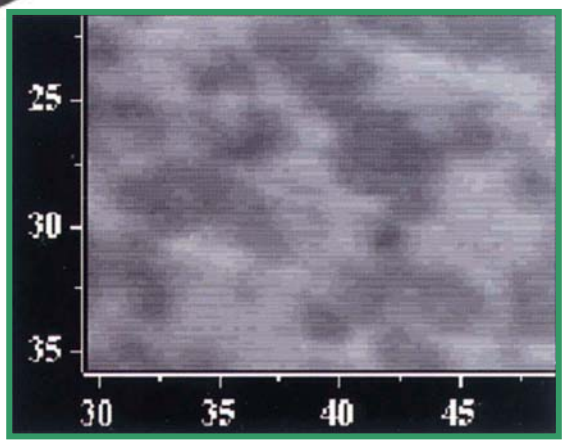
A summary of the diagnostic spectral features follows. PBT has bands at 1615 and 1735 cm^{-1} that are diagnostic of the aromatic ring and carbonyl groups; it also has CH bands above 3100 cm^{-1} indicating non-saturated organics. Fingerprint bands at 1060, 1130, and 1300 cm^{-1} and the CH band between 2800 and 3000 cm^{-1} are typical for PE. The difficulty in obtaining a pure spectrum of PE could be interpreted to indicate a certain degree of miscibility of PBT in PE. Note that these spectra were recorded in a matter of seconds on the LabRAM, making characterisation of these polymer blends easy enough for routine measurements.

Chemical Mapping of Phases

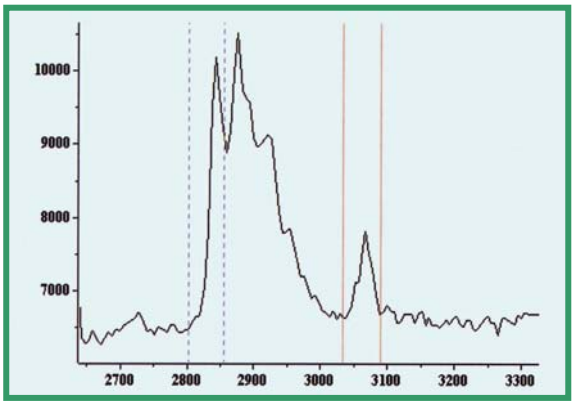
Confirmation of chemical identity of the two phases with the transparent and opaque material in the TV image can be further clarified with a Raman map.

On the LabRAM a confocal map can be achieved with the unique patented **confocal line scan**. With this system, one multiplexes the line-illumination on the sample by focusing a spectrum from each point on that line on to a track on the CCD. Consequently, the full spectrum from each sample point is stored. After the spectral acquisition, one can examine the full file, and select the analytical band in the spectrum from which an image can be reconstructed. Alternatively, one can .model. spectra by creating maps where the species. intensities are correlated by the full spectra, not individual bands.

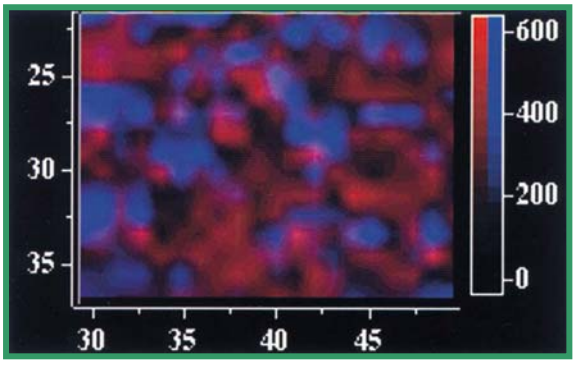
This figure shows a TV image of an area approximately 15x15 μm^2 from which a Raman chemical map was reconstructed.



The CH spectral region here is convenient for reconstruction of the map. The line at 3075 cm^{-1} (unsaturated CH) comes from the PBT phase, and the line at 2860 cm^{-1} from PE.



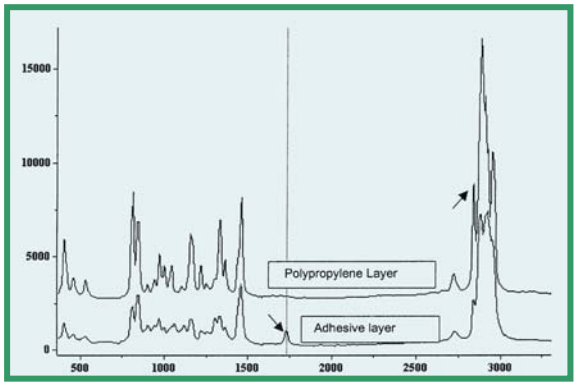
By selecting these Raman bands with cursors, the LabSpec software creates a map showing the PBT in red and the PE in blue.



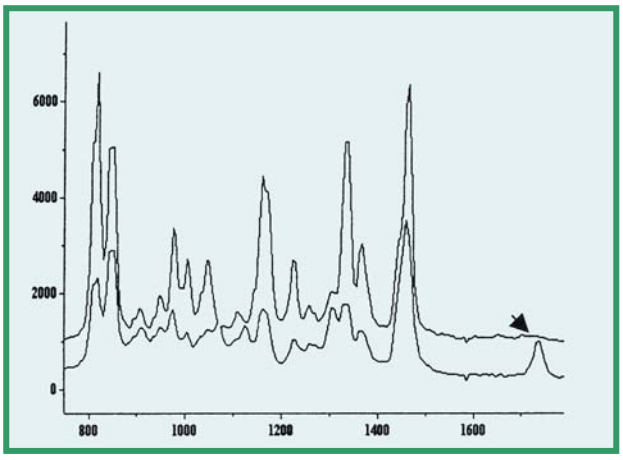
Careful comparison of the TV image and Raman map shows a less than perfect correspondence between the two images. This is, in fact, a result of the imperfect partitioning of the two phases that was already apparent from the microprobe study.
The Raman map created by the LabRAM provides more detailed information on the chemical distribution of the polymer species in this blend than could be achieved with a TV image and a Raman microprobe without mapping capabilities. One sees that the fields with the purest PBT
(red) are larger than the regions with pure PE (blue). In addition, the largest domains show mixed spectra, but there are many abrupt frontiers.

Raman Chemical Depth Profiling With Automated Z Focus

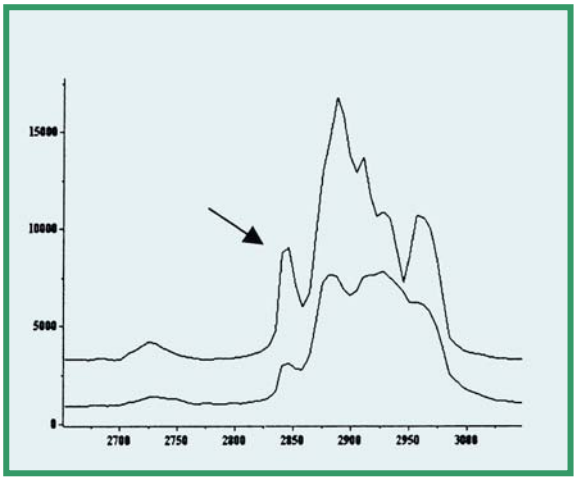
Depth profiling of a multi-layered structure
A confocal Raman microscope can be used to depth profile a multi-layered structure. In this example, stacking several layers of adhesive tape on a microscope slide produced a multi-layer structure for test purposes. The tape used was of the pressure sensitive type consisting of a continuous polymer film with a glue layer on the bottom side. Below are the spectra of the polymer film and the adhesive layer. By comparing the spectrum of the film to reference polymer spectra, the film is identified as isotactic polypropylene of medium crystallinity. Similar comparisons indicate that the glue layer consists of low-crystallinity,
atactic polypropylene (note the inversion of the peak intensities at 820 cm^{-1}) with some short polyethylene sequences (1305 cm^{-1}), and an
ester carbonyl (1727 cm^{-1}). Thus the glue layer most likely consists of a partially esterified ethylene-propylene copolymer.

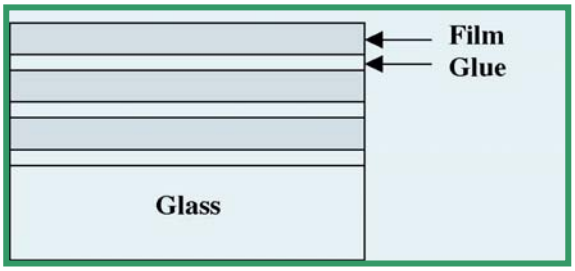


The arrows indicate bands that were used for profiling. The carbonyl band of the adhesive layer appears in a spectral region where there are no bands of the polymer film. Most of the intensity of the CH band at 2836 cm^{-1} is attributed to the
polymer film. These are the analytical regions of the spectra showing more detail.



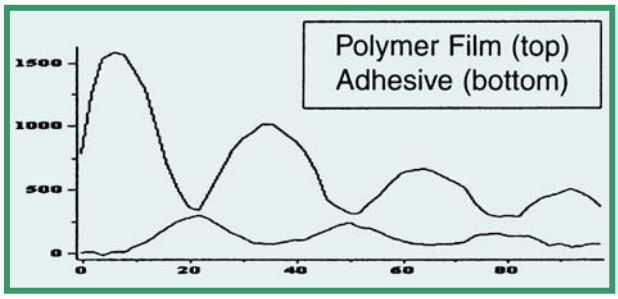
The multilayer sample structure is represented in this figure.

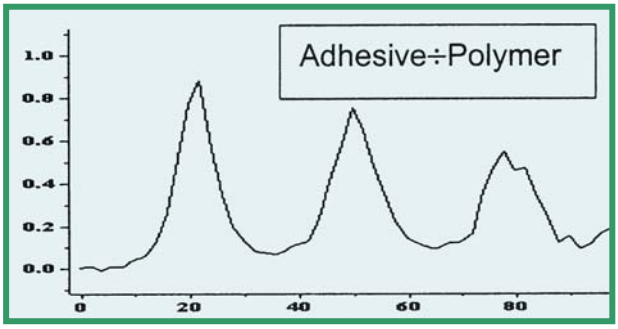




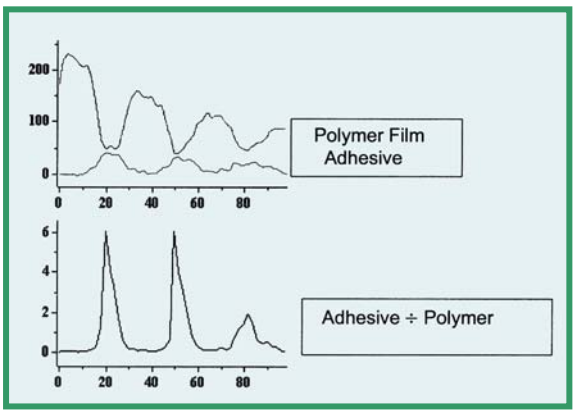
In the LabRAM spatial filtering is achieved by closing a computer controlled, variable aperture, confocal pinhole. Depth profiles are acquired automatically with the piezo focus objective. For demonstration purposes, two profiles are displayed: one with the pinhole open to 1000 µm diameter (and therefore without spatial filtering), and one with the pinhole set to 100 mm diameter (for good spatial filtering).
When spectra are acquired with the 100x microscope objective, the depth resolution has been shown to be 2-3 µm [1,2]. The following profiles represent 50 spectra collected at 2 µm spacings, starting at the surface of the stack.

Depth profile with confocal hole set to 1000 µm
The profiles on the top of this next figure represent the integrated intensities of the Raman analytical bands of the respective components. The bottom of the figure shows the ratio of the Raman band areas.





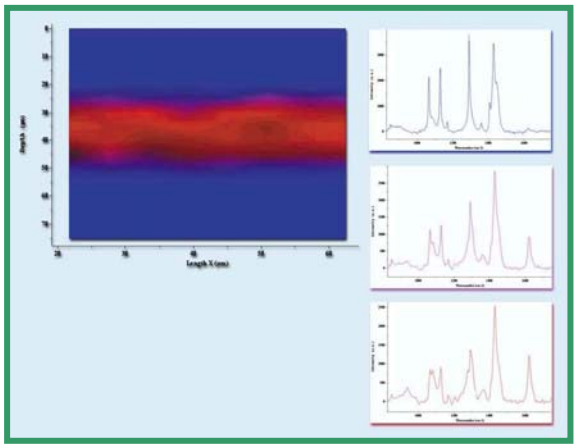
Depth profile with confocal hole set to 100 µm
These depth profiles were acquired with the confocal hole set to 100 µm for better definition of the layers. The somewhat noisier profiles result from the reduction in signal to noise that occurs when the confocal hole is closed and the signal is reduced because the effective volume generating the Raman signal is reduced. However, the important point is the reduction in the FWHM (full width at half maximum) of the profile of the adhesive signal divided by the polymer signal.



Its value is improved from about 9 µm in the first layer when the confocal is open, to about 6 µm in the first layer when the confocal hole is set to 100 µm. Looking at these profiles, one also sees that the spatial resolution seems to degrade deeper in the sample. The loss in spatial resolution when probing deep within a sample has been studied more fully since this work was originally done in 1997. This behaviour results from the optical correction of the microscope optics being done for air (index = I) whereas the tape has an index closer to 1.5.

Cross-sectioning of a laminar sample
The following results concern the analysis of a 75µm-laminar film made of 2 layers of polyethylene sandwiching a middle nylon layer. Mapping in the XZ plane was carried out by recording spectra by point imaging along a line in the X direction and repeating that at different depths separated by 5µm. This provides the same type of information as the measurement over a cross section of the sample but does not require any sample preparation; in this case this could be quite important because of the difficulties encountered in microtoming polymers. The results shown in the figure 10 illustrates the confocal approach when high depth spatial resolution is required.
Both depth profiles and cross-sectioning of polymer laminated films have demonstrated the confocality and high Z-discrimination of the LabRAM.'s Raman microprobe. It is important to recognise

that the depth profiles were performed through transparent or even semi-transparent layers up to 100 µm below the surface. Using these results, chemical and structural information can be extracted without sample preparation (ie., no microtoming, etc.). The technique can also be applied to study dynamic problems such as following a curing front or diffusion through a complex sample.



1 - L. Markwort, B. Kip & B. Roussel, Appt. Spectrosc., 49 (1995), 1411

2 - R. Tabaksblat, R. Meier & B. Kip, Appl. Spectrosc., 46 (1992), 60

3 - Modelling and Measuring the Effect of Refraction on the Depth Resolution of Confocal Raman Microscopy, Neil J. Everall, Appl. Spectros. 54, 6, pp 773-782 (2000)

4 - Confocal Raman Microscopy: Why the Depth Resolution and Spatial Accuracy Can be Much Worse than You Think, Neil J. Everall, Appl. Spectrosc., 54, 10 pp. 1515-1520 (2000)

HORIBA JOBIN YVON

France : HORIBA Jobin Yvon S.A.S., 231 rue de Lille, 59650 Villeneuve d'Ascq. Tel : +33 (0)3 20 59 18 00, Fax : +33 (0)3 20 59 18 08. Email : raman@jobinyvon.fr www.jobinyvon.fr
USA : HORIBA Jobin Yvon Inc., 3880 Park Avenue, Edison, NJ 08820-3012. Tel : +1-732-494-8660, Fax : +1-732-549-2571. Email : raman@jobinyvon.com www.jobinyvon.com
Japan : HORIBA Ltd., JY Optical Sales Dept., 1-7-8 Higashi-kanda, Chiyoda-ku, Tokyo 101-0031. Tel: +81 (0)3 3861 8231, Fax: +81 (0)3 3861 8259. Email: raman@horiba.com
Germany: +49 (0) 6251 84 75-0 **Italy:** +39 02 57603050 **UK:** +44 (0)20 8204 8142
China: +86 (0) 10 6849 2216

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