

# Raman microscopy of synthetic fibres

par G.D. Ogilvie and L. Addyman (ICI Fibres, Harrogate, North Yorkshire, G. B.)

## Microscopie Raman de fibres synthétiques

Des défauts dans les filaments textiles, se produisant lors du filage en phase fondue, amènent la réussite de la fabrication des fibres synthétiques de bonne qualité. La gravité du problème des défauts dans les filaments augmente en fonction de la vitesse croissante de production et de la diminution du diamètre des filaments. L'analyse de tels défauts et leur élimination est d'une importance primordiale pour le fabricant.

Les défauts dans les filaments peuvent être classés suivant leur origine :

1. Inclusions, dans le filament, de particules contaminant le polymère utilisé :

1.1. Contamination « interne » par des substances faisant partie de la formule du polymère ou produites pendant la polymérisation ;

1.2. contaminations « externes » par des substances variées, acquises pendant les manègements des matériaux.

The prime consideration of a manufacturer is the continuing satisfactory and trouble-free production of a good quality product. This is especially true in the manufacture of consumer textiles from synthetic fibres produced by spinning from the molten polymer. Defects or breaks in the textile filaments can seriously interrupt or interfere with the production process and impair the quality and appearance of the textile product.

Typically the textile yarn is composed of about thirty filaments spun and wound together. For economic reasons recent technology has increased the spinning speeds from about 1 200 metres/minute to speeds in the region of 6 000 metres/minute. At the same time the diameters of the individual filaments have decreased to 5-20  $\mu\text{m}$ . The elimination of filament breaks caused by particulate contamination of the polymer has become increasingly more important when the contaminant can form a substantial proportion of the material flowing through the spinneret. This has led to the development and application of more sophisticated methods for detecting and analysing such particulate contaminants so as to eradicate them. Special assemblies of filters with the spinning pack remove particulate matter down to the 5  $\mu\text{m}$  size range. The lives of these assemblies (as measured by the rate of increase in pressure within the spinning pack) have considerable significance in the production economics. Accordingly the analytical tools must function in the sub-5  $\mu\text{m}$  range. In the past particulate contaminants have been distinguished by their filterability or particle size. The classical methods of optical microscopy have also provided invaluable information. But characterisation of its chemistry is usually necessary to identify the material and establish its source. In ICI for some time we have used a laser microprobe in conjunction with an emission spectrograph to define the elemental compositions. The Raman microprobe Mole is now providing molecular information from which the contaminant and its origin can be identified.

Filaments defects can be classified according to their origin :

1. Inclusions in the filaments arising from particulate contamination of the feedstock polymer ;

These can be sub-divided :

1.1. « internal » contamination from substances present as part of the polymer recipe or produced during the polymerisation,

1.2. « external » contamination from miscellaneous substances acquired during the materials handling processes ;

2. Morphological inhomogeneities produced in the filaments at spinning or drawing.

A filament break caused by an inclusion is shown in photo 1. In this

2. Des hétérogénéités morphologiques produites dans les filaments pendant le filage ou l'étirage.

La microsonde Raman à laser Mole est un nouveau et important instrument pour l'identification de particules contaminant les fibres filées en phase fondue et la détermination de leur origine. Plusieurs exemples seront donnés.

La microsonde Mole a fourni des informations nouvelles sur la structure moléculaire et la morphologie localisée d'un filament filé en phase fondue. Quelques expériences consacrées à l'étude de l'ordre et de la géométrie moléculaire dans des filaments de polyéthylène téréphthalate seront décrites.

Des limitations théoriques et expérimentales seront exposées succinctement.

work it is usual to examine the broken filaments under normal and polarised white light (photo. 2). Note the swelling of the filament towards the break and the birefringent streak.



Photo 1.



Photo 2.

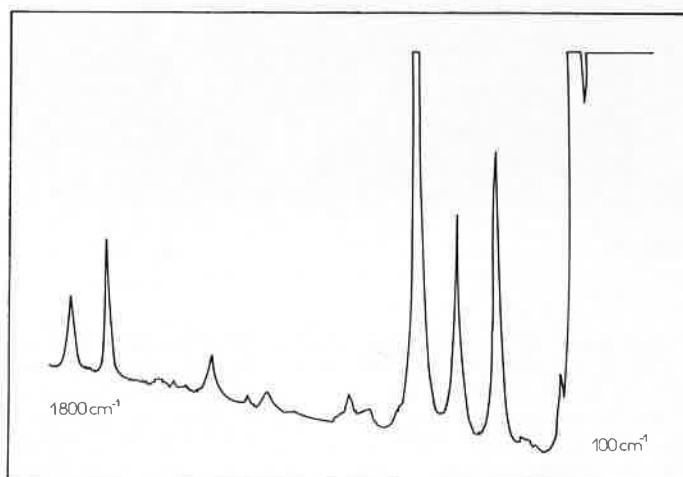


Figure 1.

The inclusion which caused the break was identified from its Raman spectrum as titanium dioxide (Figure 1). Its distribution along the filament was studied from the Raman image at  $140\text{ cm}^{-1}$  (photo. 3).

The titania forms part of the polymer recipe, its function being to reduce the lustre of the textile yarn. With the development of surface coated titania in recent years the tendency of the  $\text{TiO}_2$  to form agglomerates has been much reduced. However the reactor conditions sometimes lead to the breakdown of these surface coatings, deposits form on the spinneret (photo. 4) and these cause the broken filaments.



Photo 3.

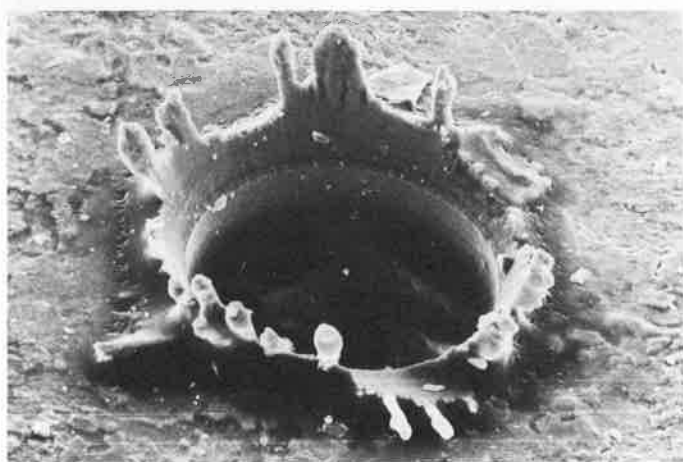


Photo 4.

Figure 2 shows Raman spectra obtained on the Mole of such deposits. They distinguish normal polyester polymer, degraded polymer,  $\text{TiO}_2$  and the surface coating. The characteristic spectrum of carbon should be noted. A particular advantage of the Raman microprobe in this work has been its ability to identify and characterise carbon. This has enabled us to distinguish carbonaceous residues produced in the thermal degradation of polymer from the activated carbons used in the process.

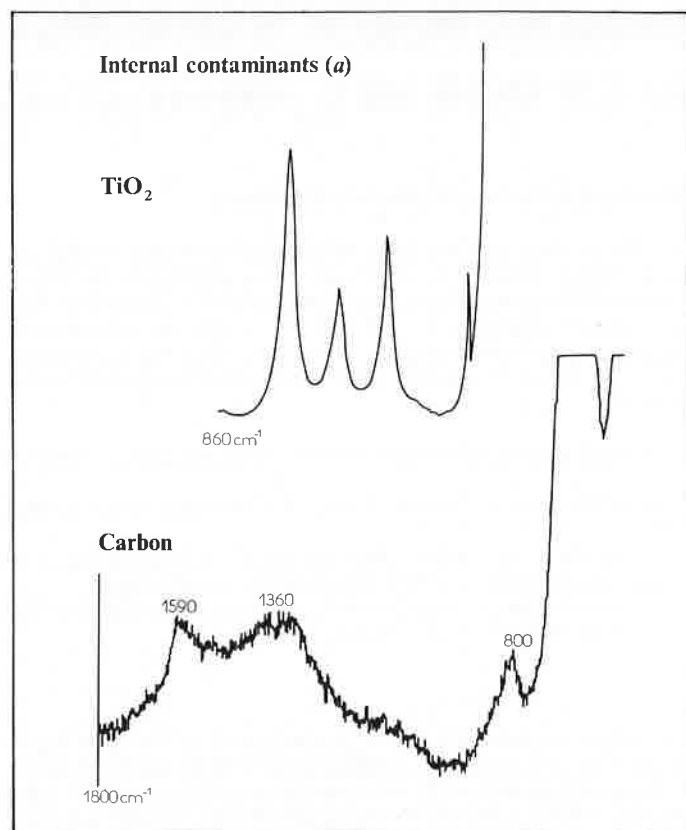


Figure 2. a.

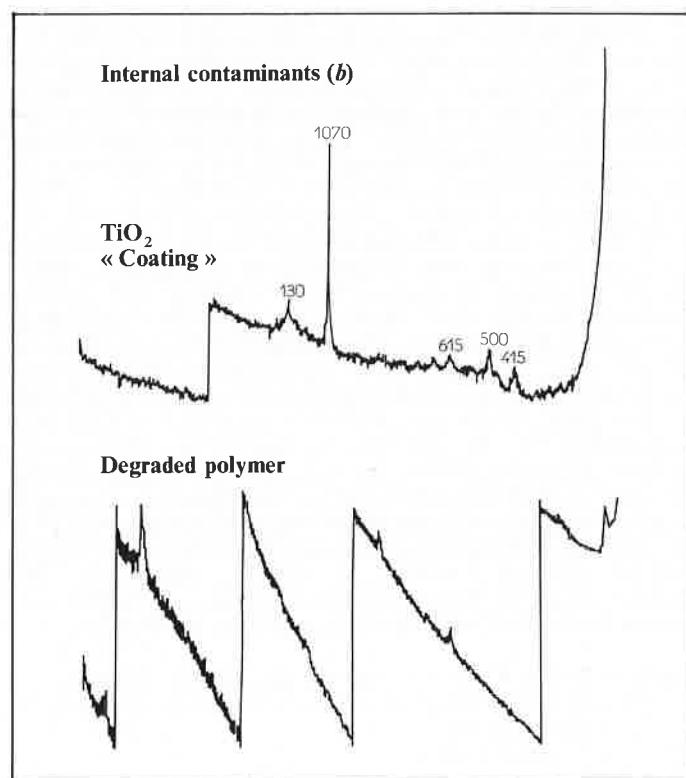


Figure 2 b.

It is particularly vulnerable during the stages which involve handling the raw materials and intermediates. In theory any form of « external » contamination might be encountered. In practice the materials most frequently observed include *packaging materials*

(cellulose derivatives, polyolefines, polyvinyls, insulation materials, fibreglass, asbestos) and *miscellaneous debris* (workers' clothing, air-born dust).

Mole spectra of such particulates found in our own work are shown on figures 3.

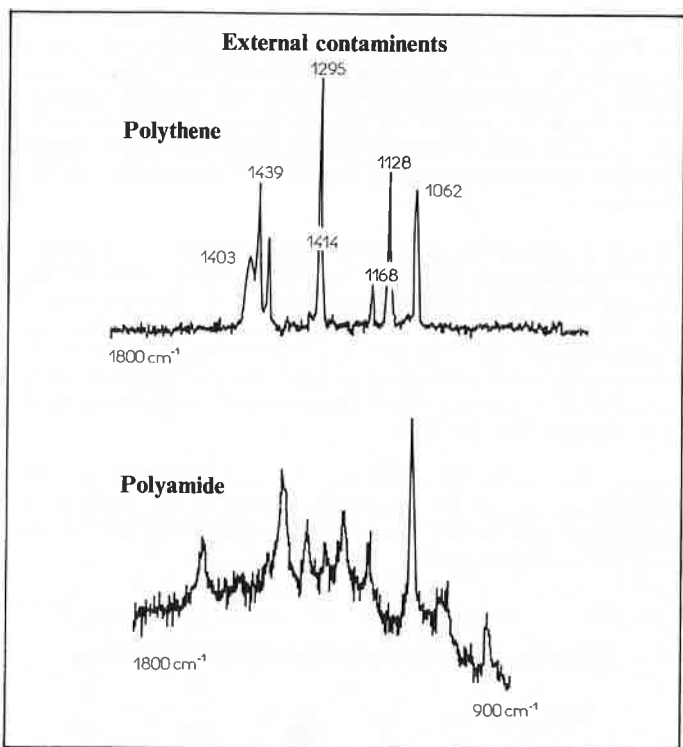


Figure 3 a.

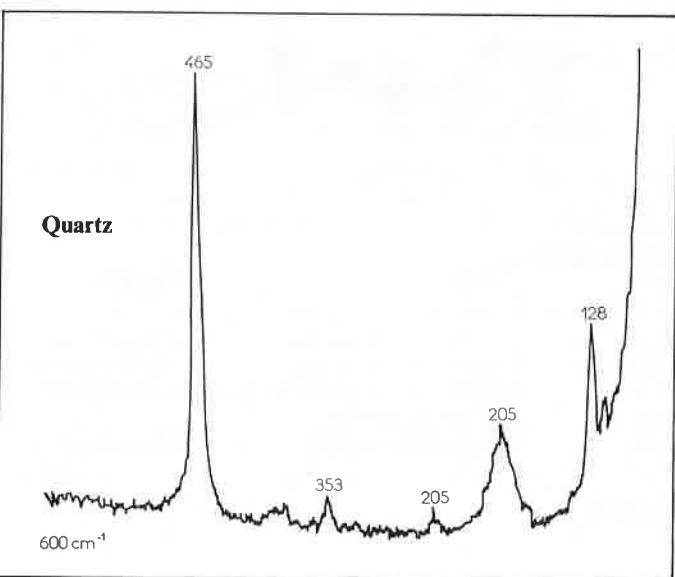


Figure 3 b.

A major problem in obtaining Raman spectra of these contaminants has been fluorescence, the bugbear of Raman spectroscopy. However the Raman microscope has shown that fluorescence is sometimes localised and also degraded locally by continuous irradiation with the laser beam. Using the Mole in the imaging mode we have been able to locate fluorescent and non-fluorescent areas within the same, otherwise homogeneous, sample and obtain useful spectra (photo. 5 et figures 4).

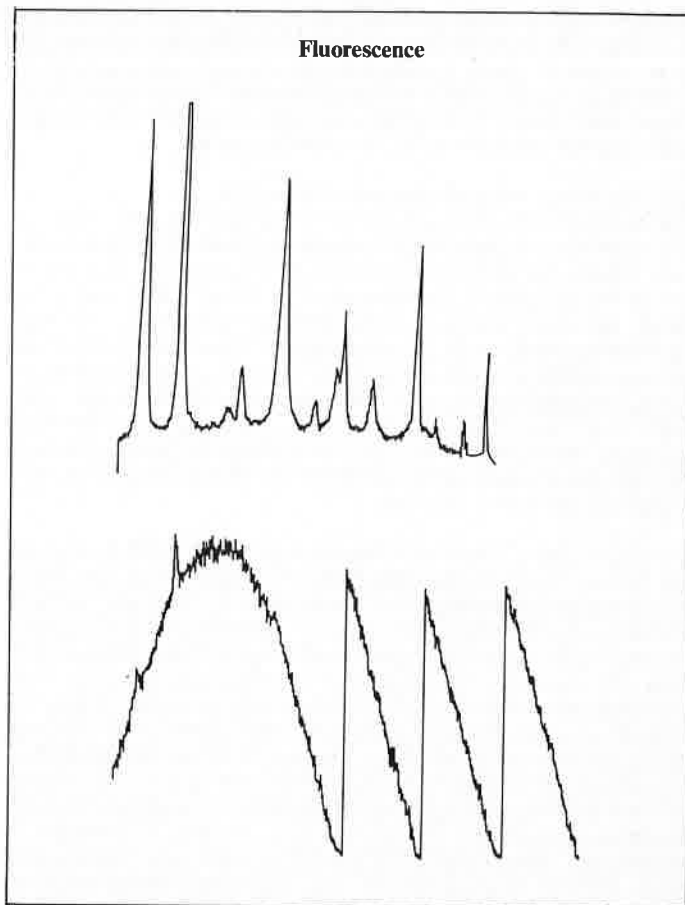


Figure 4.



Photo 5.

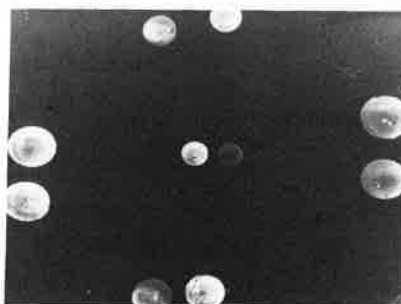


Photo 6.



Photo 7.

However there have been samples from which we could not obtain a spectrum, even after continuous laser irradiation for 24 hours or more. Photo. 6 shows a spherical contaminant isolated from a polyester yarn and photo. 7 shows its fluorescent image on the Mole. Other spectroscopic technics have revealed that it is a sulphonated vinyl benzene polymer viz, an ion exchange resin.

This has been a notable failure for the Mole !

Fluorescence will continue to be a problem in the study of thermoplastic polymers which contain localised areas of degradation. This has inhibited our work on polymer gels which are a major source of « internal » contamination in fibre-forming polymers. These gels are formed by cross-linking mechanisms and they encompass a wide range of compositions. From relatively normal polymer networks which are colourless and soluble they range to highly cross-linked networks which are amber in colour and only swell in solvents. The characterisation of these gel particles is of particular importance to us since they are deformable and will pass through the spinning pack assemblies and the spinnerets but still impair the quality of the yarn.

Our knowledge of the Raman spectra of these gels is still developing but we have made some progress. When looking at photo. 2 we noted a birefringent streak along the polyester filament. The band-width of the Raman carbonyl band at  $1\ 730\ \text{cm}^{-1}$  recorded with the laser spot focused within the streak is significantly narrower than that recorded with the laser spot focused in the non-birefringent areas. This indicates the streak contains polymer with a higher degree of crystallinity. Polymer within the streak also showed the abnormal solution properties associated with gel and we reason that the higher crystallinity is produced by the strains experienced by the gel particles during their flow and deformation through the spinning assemblies and in the molten threadline. Another explanation is annealing of the gel within the reactor or melt pool. There is still much work to be done in this area of polymer spectroscopy to establish the spectra-structure correlations of cross-linked polymer networks.

For characterising the morphology in oriented polymers such as synthetic fibres, however, Raman spectroscopy is invaluable. When considering the polyester gels I referred to the measurement of crystallinity from the carbonyl band-width. This is greater the less crystalline the polymer and it is associated with departures from planarity of the benzene rings. Figure. 5 shows the good correlation between the Raman measurements, on the Mole, and measurements of density.

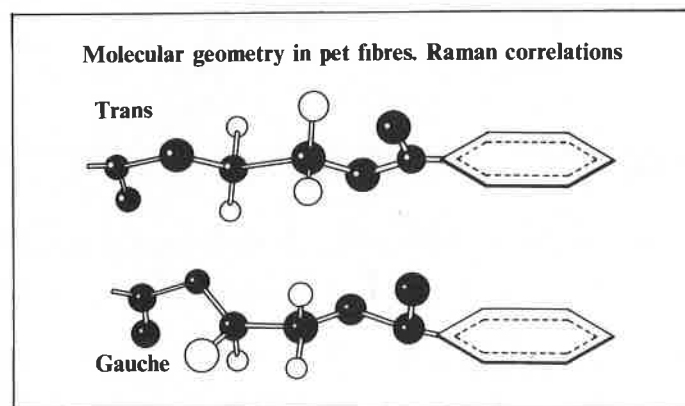
To improve the mechanical properties of the fibre it is stretched or drawn during production to orient the molecules so that the chain

axes are preferentially oriented towards the fibre axis rather than being at random. In order to understand the properties of the fibres it is necessary to study the conformation of the molecule and the chain orientations and the ways in which these vary when the fibre is subjected to the stretching and shrinking processes of the textile science. The Raman spectrum can provide this information if polarised radiation is used.

Such orientation measurements have been well described by Ward and Bower at the University of Leeds and there will not be time to develop the theoretical treatment here. Briefly the complex Raman scattering function simplifies for polymers with uniaxial symmetry such as fibres. For a fibre the Raman scattering depends on the distribution of orientations only through  $(\cos^2\theta)$  and  $(\cos^4\theta)$  where  $\theta$  represents the angle between the molecular chain axis and the draw direction.

We have been studying the orientation in filaments of polyethylene terephthalate using the band at  $1\ 616\ \text{cm}^{-1}$ . When comparing data obtained on the Mole with data obtained on another spectrometer with conventional optics, the values of the orientation functions obtained on the Mole are much less than the expected values. We believe these errors are caused by scrambling of radiation by the beam-splitter in the Mole. I welcome any views on such polarisation measurements with the Mole.

Despite this problem the Raman spectrum does provide good information about the molecular geometry in filaments of polyethylene terephthalate. Come useful spectra-structure correlations are listed in figure 6.



| Raman band $\text{cm}^{-1}$ | Mode                         | Response         |
|-----------------------------|------------------------------|------------------|
| 1 730                       | C=O stretching               | crystallinity    |
| 1 616                       | ring C—C stretching          | Orientation only |
| 1 120                       | ring C—H in-plane bending    | conformation     |
| 1 097                       | C—O stretching               | + orientation    |
| 886                         | glycol $\text{CH}_2$ rocking |                  |

Figure 6.

## Bibliography

- (1) A. J. Melveger, Laser-Raman study of crystallinity changes in PET. *J. Poly. Sci.*, 1972, **10**, 317.
- (2) J. Purvis and D. Bower, Molecular orientation in PET by means of Laser-Raman spectroscopy., *J. Poly. Sci.*, 1976, **14**, 1461.
- (3) I.M. Ward, The measurement of molecular orientation in polymer by spectroscopic techniques, *J. Poly. Sci., Poly. Symp.*, 1977, **58**, 1.

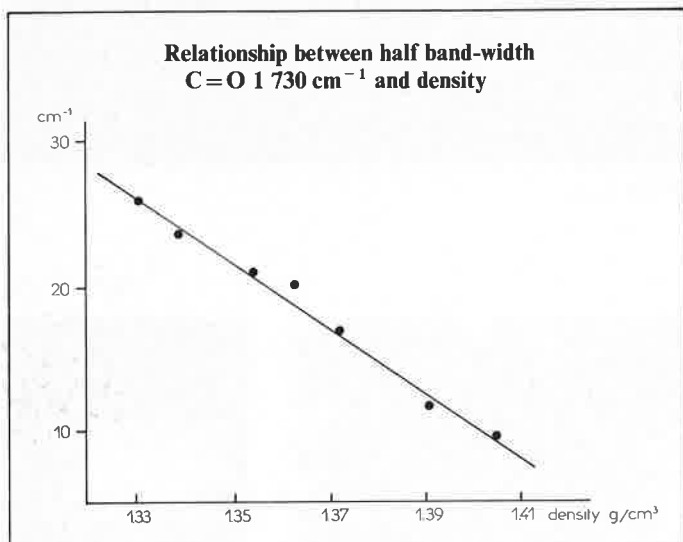


Figure 5.