



The Use of FT-Raman Spectroscopy and Chemometric Procedures in the Analysis of Polymers

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INTRODUCTION

Infrared spectroscopy is one of the major analytical techniques in industrial polymer laboratories. Conventional Raman spectroscopy, although historically used extensively in research applications, has never become a routine technique in this field. This is mainly due to the appearance of strong fluorescence backgrounds upon excitation with visible (i.e. high frequency) lasers. These strong backgrounds often completely overwhelm the weak Raman spectrum.

Although some pure polymeric (plastic) materials show good Raman spectra, additives, fillers, contaminants or degradation products are often present, which causes 'real' world samples to fluoresce. It is estimated that of real-life polymer samples only between 10-15% give an interpretable Raman spectrum when lasers of 488, 514 or 532 nm are used. This makes Raman spectroscopy using visible lasers a virtually useless technique for routine applications in a polymer laboratory.

In visible Raman spectroscopy several methods have been attempted to reduce fluorescence. In the polymer industry the most important one is *quenching* of the fluorescence. In this method the material is irradiated with the laser (either at a similar or at a higher power as in the real measurements) for a certain amount of time, from a couple of minutes up to several hours. It appears that the fluorescence is often minimized after this 'pretreatment'.

Of course, the material may be damaged or its properties be changed and the measurement may take very long. Furthermore, the quenching process is often not fully understood, and fluorescence may re-appear when the laser is turned off.

Another more practical approach to avoid fluorescence is the use of low frequency lasers. In this way the virtual levels (the energy level of the excited state when the molecule is irradiated with the laser) are moved away from the electronic levels. Therefore, the chance that an electronic level is excited, which is a prerequisite for fluorescence, decreases. Upon using a near-infrared laser, such as an Nd:VO₄ at 1,064 nm, the success rate in the polymer industry has increased to about 90%.

When a near-infrared laser is used, the Raman cross-section of the molecules decreases with a frequency to the power 4 factor. Therefore the amount of photons undergoing the scattering process decreases. In order to compensate for this, the Fourier Transform Raman technique has been developed, in which the advantages of an interferometer (rather than a light dispersing element such as a grating or prism) make up for the decrease in scattered radiation.

Due to the internal calibration with a He-Ne laser (Connes' advantage) the wavenumber axis (Raman shift) of an FT spectrum is very precise. Therefore, scans can be co-added in order to improve the signal-to-noise of the final spectrum. The high precision makes FT-Raman spectroscopy an ideal technique for analysis methods such as library searching, discriminant analysis or chemometric techniques where a high abscissa precision is required.

Furthermore, in FT-Raman an impression of the bulk material is obtained since the laser does not need to be focused to a very tight spot, and therefore heterogeneities are averaged out.

This note presents two applications which use FT-Raman spectroscopy and quantitative data analysis in order to determine crucial polymeric properties on a routine basis. Since sample preparation is minimal the technique offers major advantages over the existing and currently used techniques.

EXPERIMENTAL

Chemometric Methods and FT-Raman Spectroscopy

A big advantage of Fourier Transform spectroscopy – either Raman or infrared – over dispersive techniques is the high precision of the wavenumber axis. FT instruments achieve this by internal calibration with a He-Ne laser. In practice this means that spectra can be measured over long periods of time in a variety of different temperatures and atmospheric conditions without experiencing wavenumber shifts. This is of particular importance in quantitative analysis using chemometric techniques such as Partial Least Square (PLS) analysis, since such methods are very sensitive to changes in peak positions.

When using FT-Raman spectra in quantitative methods, one should be aware that the band intensities depend on several instrumental properties, such as laser power, sample position, instrumental response, etc. In order to correct for this, simple methods like 'the total integrated area is set to unity', or 'the y-axis is scaled from 0 to 1'

are often sufficient. Modern computer techniques make more sophisticated normalization procedures possible. For example, the Multiplicative Scattering Correction method, which is often used in near infrared methods, can be successfully used for FT-Raman spectra too. All normalization procedures will be affected by the fluorescence background present in the spectra, especially when its intensity varies. Therefore, other pretreatment procedures, like peak intensity ratios or first derivative spectra, may be necessary to get accurate and reproducible results.

Determination of Crystallinity of Poly(ethyleneterephthalate)

Poly(ethyleneterephthalate) is a common polymer used in the packaging industry (plastic bottles). Its structure is depicted in Figure 1.

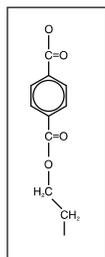


Figure 1. The chemical structure of Poly(ethyleneterephthalate)

As in any polymeric material several structural features determine the mechanical properties of PET. These include conformations, orientation, crystallinity, etc. A thorough knowledge and understanding of these properties is important. For this reason, analytical methods which can determine these properties are under constant investigation.

Currently, the crystallinity of PET is determined with either gradient density column measurements, infrared spectroscopy or x-ray diffraction. However, many of these techniques require that the sample be cut, ground or put under pressure to be analyzed. In preparing the sample, its properties may change. FT-Raman spectroscopy does not require sample preparation, so a chip or film can be placed directly into the instrument and therefore shows a lot of promise.

The Nicolet FT-Raman instrumentation allows the user to vary the laser power at the sample from 0 to 1.5 Watts. As stated above, heat may change the properties of the material. The heat induced by the laser may thus anneal the samples. In the project described here it was found that a laser power of 300 mW (or less) did not cause any visible changes in the FT-Raman spectrum over a time period of 30 minutes. Due to the very efficient optical path of the

Nicolet Raman instruments, even at lower laser powers, a very high signal-to-noise is obtained. The signal-to-noise of the final spectrum is a very important factor in the accuracy of a quantitative method. The spectra were measured on a Nicolet FT-Raman 960 stand-alone instrument with Ge detector, 64 scans at 16 cm^{-1} (measurement time: ~ 30 seconds).

The film samples were clamped in the gold-coated film holder which could be reproducibly re-positioned in the instrument. No further sample preparation was performed.

The FT-Raman spectra of crystalline and amorphous PET are shown in Figure 2. The assignment of the bands which are sensitive to crystallinity and/or conformation (*trans* and *gauche* conformers of the glycol unit) is well-established. It is described in the literature that the bandwidth of the C=O stretching region can be used as an indication for the crystallinity (order) of the material, and that the bands at 1096 and 1000 cm^{-1} are associated with the *trans* conformer of the glycol unit. However, the interpretation is complicated by the fact that the degree and direction of the molecular orientation (chain conformation) also affects the spectrum due to the fact that the laser is often polarized in FT-Raman instruments.

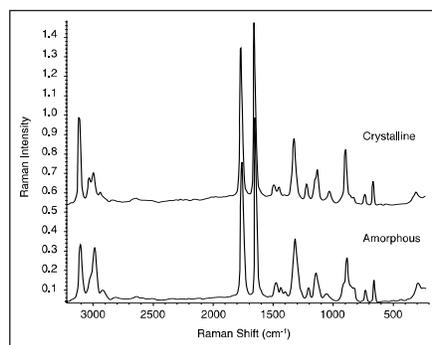


Figure 2. FT-Raman spectra of crystalline and amorphous Poly(ethyleneterephthalate) films. Measurement conditions: Laser power 300mW; 64 scans at 16 cm^{-1} resolution (~ 30 seconds measurement time).

In order to control or change the crystallinity of polymer samples, they can be annealed (the sample is heated to a certain temperature and then cooled down with a specific rate), or drawn (the sample is drawn with a certain force in 1 (uni-axial) or 2 (bi-axial) direction(s)). The crystallinity of the PET samples which were used in this study was changed by drawing the samples, rather than annealing them. When samples are annealed (heat-treatment) the

orientation of the polymer chains is hardly affected. Drawing a polymer sample can result in physical property changes which are dependent on the sample's orientation. The samples used in these measurements can be divided in 2 groups: 6 low crystallinity samples which were drawn uni-axial, and 7 high crystallinity samples which were drawn bi-axial. All of the samples were measured with (one of) the drawing axes parallel to the polarization of the laser in order to minimize orientation/polarization effects. The spectra were normalized by scaling them from 0 to 1 unit in the intensity axis.

RESULTS AND DISCUSSION

In order to predict crystallinity from the measured spectra, we built a quantitative method using the regions described in the literature: $1820\text{-}1666\text{ cm}^{-1}$ for carbonyl stretching and $1160\text{-}950\text{ cm}^{-1}$ for glycol. We were able to simply account for the slight background present in the spectra by using first derivative spectra in the method.¹

Figure 3 shows the cross-validation plot upon using 3 factors where the lowest PRESS (Predicted Residual Error Sum of Squares) value was found. A minimized PRESS is a good indication for the accuracy of the method. In cross-validation procedures, the method is built by leaving one spectrum out, building the model using the remaining spectra and then using this model to predict the one which was left out. This is repeated for all spectra. This kind of cross-validation gives an impression of how valid the method will be for predicting the values for unknown samples – this after all is the reason for constructing a quantitative method. The method determined here with $\text{RMSP} = 0.0017\text{ g cm}^{-3}$

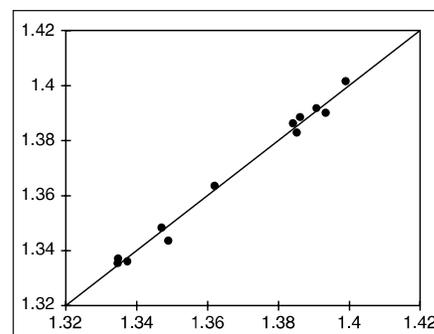


Figure 3. Cross-Validation Prediction Plot of PLS calibration using PET samples with (one of) the drawing axes parallel to the laser polarization. Analysis conditions: 3 factors used, regions $1820\text{-}1666$ and $1160\text{-}950\text{ cm}^{-1}$. $\text{RMSP} = 0.0017\text{ g cm}^{-3}$.

(Root Mean Square Error of Prediction), compares very well to calibrations described in the literature.

PLS methods when provided with adequate input data are able to model and correct for effects which are not directly related to the property in which the user is interested. Since the samples used in this method were drawn, it is reasonable to expect that orientation effects may play an important role in the model. The spectral bands in the region from 1666 to 1160 cm^{-1} are affected by orientation effects and *trans/gauche* conformation ratios, and we therefore decided to build a second method using the entire region between 1820 and 950 cm^{-1} . We anticipated that this expanded analysis region might improve the validity of the method relative to our first 'narrow range' model.

Figure 4 shows the cross-validation plot generated when using the expanded spectral region. The method does indeed improve, giving $\text{RMSP} = 0.0015 \text{ g cm}^{-3}$.

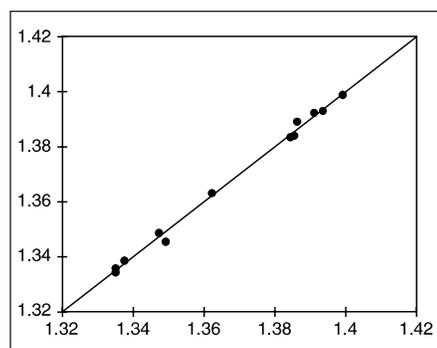


Figure 4. Cross-Validation Prediction Plot of PLS calibration using PET samples with (one of) the drawing axes parallel to the laser polarization. Analysis conditions: 3 factors used, region 1820 - 950 cm^{-1} . $\text{RMSP} = 0.0015 \text{ g cm}^{-3}$.

Further methods using even more spectral regions – both the C-H stretching region, and the region below 950 cm^{-1} – made no further improvement.

Since it is possible that the polarization of the laser has an effect on the quantitative method, it was interesting to repeat the spectral measurements with the samples oriented first parallel and then perpendicular to the laser polarization. Figure 5 shows the effect of laser polarization on the FT-Raman spectra of sample 6 which is uni-axial drawn. Besides some intensity changes, the most striking difference is the disappearance of the 1000 cm^{-1} band when the sample is placed perpendicular to the laser polarization.

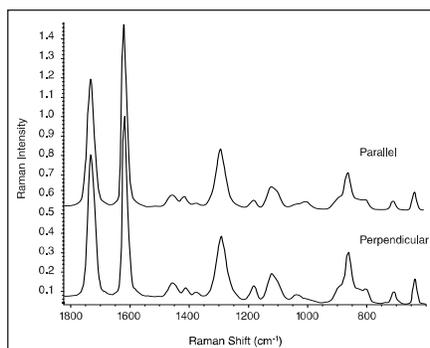


Figure 5. FT-Raman spectra of uni-axial drawn PET sample (density = 1.3491 g cm^{-3}) measured with the drawing axis parallel and perpendicular to the polarization of the laser. Measurement conditions: Laser power 300mW; 64 scans at 16 cm^{-1} resolution (~30 seconds measurement time).

A method was built from this new set of 26 spectra, using the same parameters as described above. Even when the samples were measured in both orientations, a reasonable model could be built as is shown from the RMSP values in Table 1. The main advantage of this last method is that since it is built independent of orientation, it can be used to predict unknown samples irrespective of *their* orientation.

Since the 1000 cm^{-1} band is not an absolute indication for crystallinity as can be observed in Figure 5, the method may improve when this band is left out of the PLS calibration. When this is tried for the first set of spectra (13 samples positioned with the drawing axis parallel to the laser polarization), the results of the method hardly changes. When only the carbonyl band region is used, however, the RMSP increases to 0.0023 g cm^{-3} , which is obviously worse.

It is shown here that PLS modeling can be very successful in producing a calibration for the crystallinity as expressed in density of the material, for Poly(ethyleneterephthalate). Identifiable regions of the measured spectra are sensitive to crystallinity, orientation, and maybe other properties of the material. The best calibration is obtained if the sample is positioned with its drawing axis perpendicular to the laser polarization, although it is possible to generate an acceptable method which is independent of sample orientation.

Table 1. Predicted values for different sample sets and regions

Spectra	Region (cm^{-1})	RMSP (g cm^{-3})
13	1820-1666 & 1150-950	0.0017
13	1820-950	0.0015
26	1820-1666 & 1150-950	0.0026
26	1820-950	0.0028

The suitability of this type of analysis for other polymer materials like polyethylene or poly(tetrafluoroethylene) is under investigation.

Determination of Copolymer Composition of Poly(Aryl Ether Sulphone) and Poly(Aryl Ether Ether Sulphone)

Polysulphone polymers are used in the production of separation membranes. They exhibit good mechanical properties and are very stable. The hydrophilicity, i.e. the affinity to water, depends on the level of sulphonation. During sulphonation, the hydroquinone unit is monosulphonated by treatment with sulfuric acid. Therefore, by controlling the composition of Poly(Aryl Ether Sulphone) (PES) and Poly(Aryl Ether Ether Sulphone) (PEES) copolymers, a range of different products may be produced. The chemical structure is shown in Figure 6. The ratio between PES and PEES is described with the s-number, which is defined in Figure 6.

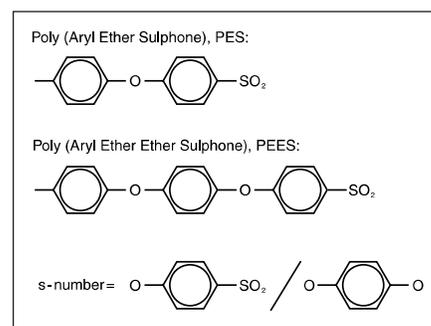


Figure 6. The chemical structures of Poly(aryl ether sulphone) and Poly(aryl ether ether sulphone).

Both FT-IR and FT-Raman spectroscopy are good techniques for the determination of the degree of sulphonation. The advantage of FT-Raman is that the sample can be measured without preparation and the operator is not required to remove the powder from the sample bottle. These benefits are important in an industrial environment both for the rate of sample throughput and for sample integrity.

For these PES/PEES copolymer samples FT-Raman measurements exhibit a

fluorescent background due to low level contaminants and additives in the mix. However, for the samples measured the fluorescence remains sufficiently weak that it does not overwhelm the FT-Raman signal, and all the samples could be used for the multivariate calibration.²

While it has been reported that uni-variate methods can be used in the determination of the copolymer composition, we expected that the accuracy of the method will increase significantly when more regions are utilized.

In the following procedure, we measured 8 samples with *s*-number varying from 2 (PEES) to ∞ – or fully sulphonated (PES). The samples were measured directly, by placing the sample bottle in the instrument compartment. The spectra were collected on a Nicolet FT-Raman 960 instrument using 300 mW of laser power and 64 accumulations at 8 cm⁻¹ (measurement time: ~1 minute).

The fluorescence background evident in Figure 7, can lead to inaccuracies in the normalization procedures used previously. Different methods were attempted to avoid these problems, such as baseline correction and derivative spectra but the prediction models developed were inaccurate.

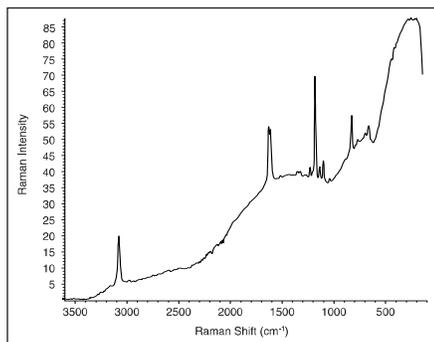


Figure 7. FT-Raman spectra of PES/PEES copolymer powder, *s*-number = 8. Measurement conditions: Laser power 300mW; 64 scans at 8 cm⁻¹ resolution (~1 minute measurement time).

Examination of the spectra (Figure 8), shows that the doublet at 1600 cm⁻¹ correlates with the *s*-number and that the strong band at 1150 cm⁻¹ seems unaffected by the change in copolymer composition. It was decided therefore to generate a straightforward model using the spectral range between 1650 and 1550 cm⁻¹, normal-

ized to the peak area of the 1150 cm⁻¹ band (calculated from 1040 to 1190 cm⁻¹). For both regions a 2-points baseline was used just outside the spectral regions of the areas of choice. This serves to accurately remove the effects of the background.

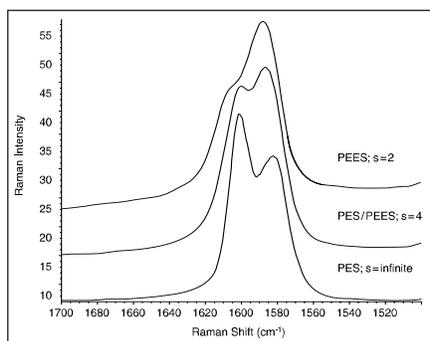


Figure 8. Effect of changing copolymer ratio of FT-Raman spectra of PES/PEES. Measurement conditions: Laser power 300mW; 64 scans at 8 cm⁻¹ resolution (~1 minute measurement time).

Figure 9 shows the cross-validation plot – a very good prediction model is obtained. Note that the predicted value, *p*, is described as

$$p = \frac{1}{s - \text{number}}$$

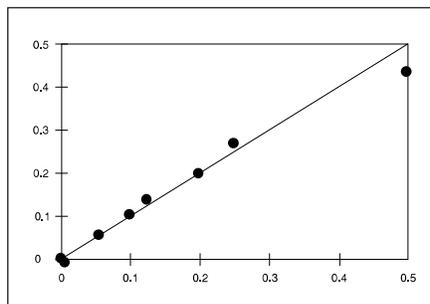


Figure 9. Cross-Validation Prediction Plot of PLS calibration using PES/PEES copolymer samples with varying *s*-number. Analysis conditions: 3 factors used, region 1650-1550 cm⁻¹, normalized to the peak area of the 1150 cm⁻¹ band.

It seems that the sample with *s*-number = 2 (*p* = 0.5) is not predicted very well. This is a common artifact of the cross-validation technique: this sample is predicted from the other standards in the method. Since it is the most extreme *s*-number, it may be seen as outside the range which can be adequately covered by the remaining samples. This, however, should not apply when the full model is used to predict an unknown – in this case, the *s*-number = 2 sample is present to represent this range of concentrations.

CONCLUSIONS

FT-Raman spectroscopy is an ideal technique for research and QA/QC analysis on polymer samples. Fluorescence problems are dramatically decreased (it is anticipated that upon the use of a near-infrared laser 90% of polymer samples gives a useable Raman spectra), and sample preparation is minimal.

Since the wavenumber axis is extremely precise upon using interferometers, quantitative analysis can be performed by chemometric techniques. The use of Partial Least Square procedures enables the user to quickly and accurately determine important polymer properties such as orientation, crystallinity and copolymer composition. The methods seem very robust, enabling the user to add more samples from different preparation methods while avoiding problems caused by sample positioning or orientation.

NOTES

1. This slight background is due to some residual fluorescence originating in low level impurities and additives present in the samples. It is of interest to note that in attempting to use dispersive Raman techniques and shorter wavelength excitation (at 488 nm) to measure these samples the fluorescence was strong enough to overwhelm the majority of the Raman signal.
2. Once again attempts to measure these samples with even red excitation at 785 nm on a dispersive system did not yield any useful Raman information.

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