



Using Chemometrics and Raman Spectra for Quantitative Predictions of Physical and Chemical Properties of Polymers

Introduction

Multivariate or Chemometrics techniques are normally applied to spectra of solutions, or mixtures of materials, in an effort to develop methods to “predict” concentrations of the various chemical species. In fact, the same mathematical techniques can be applied to elucidate physical properties as well. Actually, these two applications of Chemometrics are useful in the polymer field.

Indeed, as far as polymeric fibres are concerned, slight modifications of Raman features are directly related to differences in the molecular orientation and the degree of crystallinity of the fibres. To utilize these subtle spectral changes and correlate them with physical properties of the polymer, one is obliged to use Chemometrics on the Raman spectra.

Chemometrics also turns out to be useful when one wants to monitor polymerisation reactions. During the formation of the polymeric chains, there is almost always the loss of a double bond of the monomer structure. The Raman features associated with these double bonds are in general fairly intense, and do not mix with other bands. Therefore, by monitoring the disappearance of these particular bands, one can follow the polymerisation of the monomers. However, although the derivation of quantitative information is rather straightforward when one or two monomers are involved, it gets more complex as soon as the reactive medium contains several monomers because it becomes likely that the bands of interest from the different monomers overlap. When analytical bands overlap it becomes impossible to utilize univariate analysis of the Raman data. The use of multivariate analysis becomes then the only way to extract the valuable information.

Chemometrics applied to polarised Raman spectra of fibres of polyethylene terephthalate.

Spin-oriented and drawn polymeric fibres have applications in the textile industry and in many engineering applications (such as tire cord). The physical and chemical properties of these fibres depend not only on the chemical composition, but also on the mode of fabrication. Ultimately, the molecular orientation and % crystallinity can be related to such properties as dyeability, tenacity (strength), glass transition temperature, melting temperature, and other thermal properties such as possible % shrinkage.

It was the goal of the present study to use Multivariate Techniques to predict physical properties of PET fibres that are measured by other, perhaps more time consuming methods. The ability to predict birefringence (which is directly related to molecular orientation) and crystallinity will be demonstrated. Other physical properties that are amenable to such analysis could be dyeability (which occurs only in the amorphous regions which can solubilize the dyes), the glass transition temperature (T_g), crystallisation temperature (T_m), tenacity, draw potential before breakage, or shrinkage potential during heat treatment. The ability to predict such properties is based on the fact that they depend on:

- amorphous vs. crystalline composition
- the orientation of the amorphous material which can be monitored with the polarization dependence, and
- the conformation of the glycol bonds which can be monitored by following details in the single bond fingerprint region of the spectrum.

Raman spectra were measured with the laser and scattered polarisation in the same plane; the fibre was either oriented parallel or perpendicular to the direction of polarisation. The histories of the fibres are summarised on Table 1. One set of fibres was spin-oriented with take-up speeds (TUS) between 1500 and 5500m/min. Some of the fibres in this set were drawn at room temperature (RT) to the break point; this will further orient the amorphous material, but will not effect the degree of cristallinity. A third set of fibres was spun at 500m/min and then doubly drawn at temperatures above T_g . The properties of these fibres are tabulated in Table I.

The polarised Raman spectra of fibres of PET (fig.1) have been used to monitor orientation, cristallinity, and conformation of the glycol single bonds.

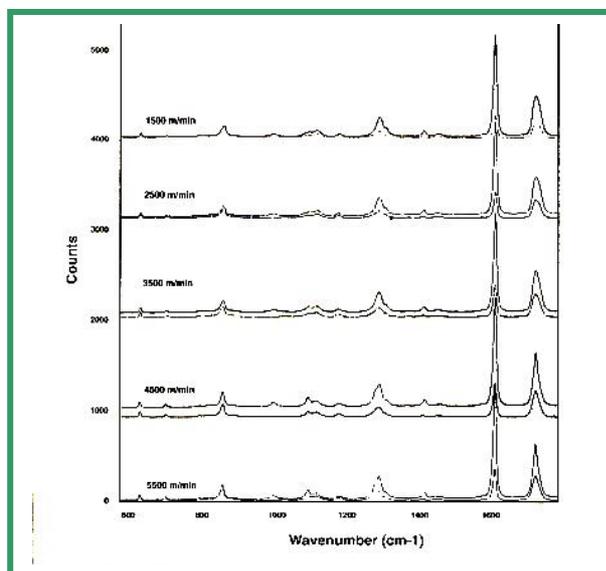


Figure 1 : Polarised Raman microprobe spectra of spin-oriented fibres of polyethylene terephthalate after room temperature draw.

The interesting characteristics of these spectra can be summarized as follows:

- The differences between the ZZ and RR spectra increase with TUS and/or draw ratio (ie., birefringence),
- The $>C=O$ band at ca. 1730 cm^{-1} sharpens in the crystalline phase, and
- The behavior in the glycol region ($950\text{--}1200\text{ cm}^{-1}$) reflects the conformation of the single bonds which correlates with orientation, but not necessarily cristallinity.

TUS (m/min)	Birefringence	Crystallinity	C=O FWHM (cm^{-1})
Spun Fibres			
1500	11,2	0	25
2500	24,9	0	25
3500	47,3	0	26
4500	75,2	11,1	22
5500	107,4	23,7	17
Spun Fibres Drawn at Room temperature*			
1500	163,5	(0)	25,5
2500	153,5	(0)	25,3
3500	147,5	(0)	24
4500	135,7	(11,1)	17
5500	125,0	(23,7)	17,8
Birefringence Measurements made by Mike Jaffe at Hoechst-Celanese			
Fibres Spun and drawn at 90 and 150°C			
500 3.8X	205,0	29,1	18,2
500 4.2X	207,7	29,5	18,3
500 4.6X	203,9	31,7	19,2
500 5.0X	213,0	26,9	19

Table 1: Histories of the different sets of fibres

At the beginning of an application of Multivariate Analysis, one needs to consider what spectral pre-treatments are necessary. Initially it was assumed that we would use the ZZ spectrum divided by the RR spectrum since Raman spectroscopists usually work with polarisation ratios. However, it is immediately apparent that such spectral manipulations will certainly cause "divide by zero" errors. Further consideration prompted recognition of the relationship of birefringence to Raman polarisation difference. Successful Multivariate Analysis resulted from use of the ZZ minus RR spectra. Other protocols are also certainly possible, but were not explored in this study.

Modelling the birefringence with a PLS algorithm was always successful ($R^2 > 0.96$); usually only 2 factors were necessary to account for most of the variance. Changes in the Chemometrics data treatments resulted in fine-tuning the model. Models based on the full fingerprint spectrum ($600\text{--}1800\text{ cm}^{-1}$) were better than models based only on the glycol single bond region of the spectrum. Clearly the birefringence depends on the relative intensities of the bands in the full spectrum as well as the conformation in the more flexible parts of the polymer chains.

Modelling the crystallinity of these fibres was less successful, possibly because 6 of the 14 fibres in the training set were non-crystalline (cristallinity = 0).

As an alternative, the crystallinity was modelled indirectly by modelling on the full width at half maximum (FWHM) of the carbonyl band from the summed spectral since this band is known to correlate with crystallinity in aromatic polyesters. Using the spectral region from 1550 to 1785 cm^{-1} produced the best model. In this case 4 factors were necessary to account for the variance, producing an R^2 value of 0.959.

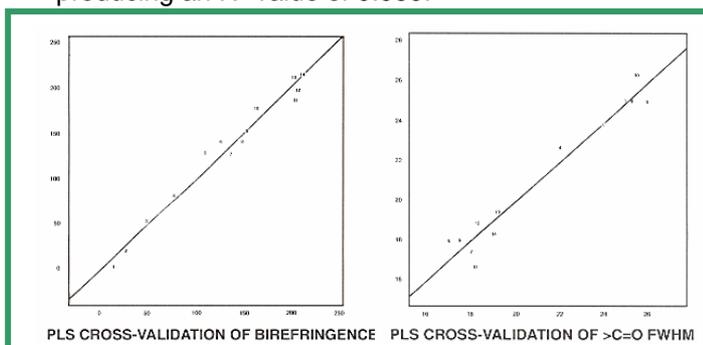


Figure 2 : Cross-validation results showing the consistency of the modelling

Since this work was originally published, other groups at Dupont Experimental Station and Clemson University have shown that it is possible to monitor these properties on spinning lines, and to follow the morphological changes as a function of distance from the spinneret jet.

Chemometrics applied to on-line monitoring of polymerisation reactions

Polymerization reactions are based on complex processes that are somewhat difficult to predict via mathematical models, especially without experimental data. Therefore, in order to improve and control the polymerization processes, the use of an accurate and fast on-line analysis technique is of great importance.

Raman spectroscopy is very sensitive to vibrations of carbon double bonds of the monomers that are consumed during the polymerization process. Therefore, monitoring the intensity of their associated Raman features allows one to follow the evolution of the reaction.

The results of a co-polymerization reaction of 90% vinyl di-chloride (VC_2) and 10% methyl acrylate (ACM) will be shown. A NIR excitation was used in order to avoid fluorescence emission, and a new adjustable immersion probe (fig.3) significantly improved the results.



Figure 3: SuperHead equipped with the immersion accessory

During the reaction, a software feature providing for automatic spectral acquisition every 5 minutes was implemented.

Spectra collected at various times during the reaction and reproduced in Figure 4 clearly highlight the disappearance of the C=C bonding ($1600\text{-}1650 \text{ cm}^{-1}$), thereby indicating the consumption of both monomers.

As the Raman bands associated with the C=C bond of these two monomers (fig.4) are well separated from each other (1612 cm^{-1} versus 1632 cm^{-1}), a univariate analysis based on band integration was possible.

However, to demonstrate the interest of Chemometrics when a more complex mixture is considered (band overlap), multivariate analysis was also applied to the data set.

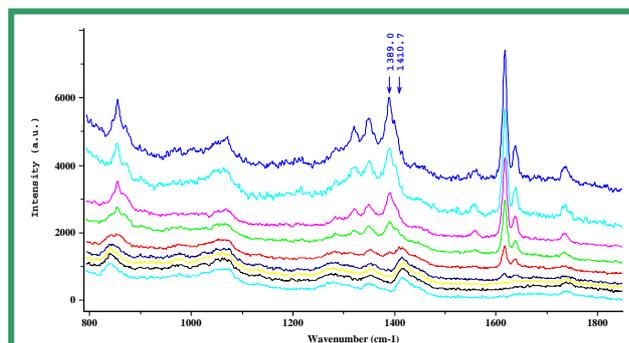


Figure 4 : Raman spectra at different times of the reaction

The Chemometrics model was built from a set of about 20 spectra selected from the total set of spectra and equally distributed over the reaction. For each spectrum, reference values of the monomers and polymer concentration were known and taken into account. The PLS_2 algorithm was used and two factors were necessary to account for the variance. This is sensitive as the co-polymer is formed from the two monomers.

The R^2 ($R^2 > 0,96$) values of the cross-validation attest to the success of the model (fig 5).

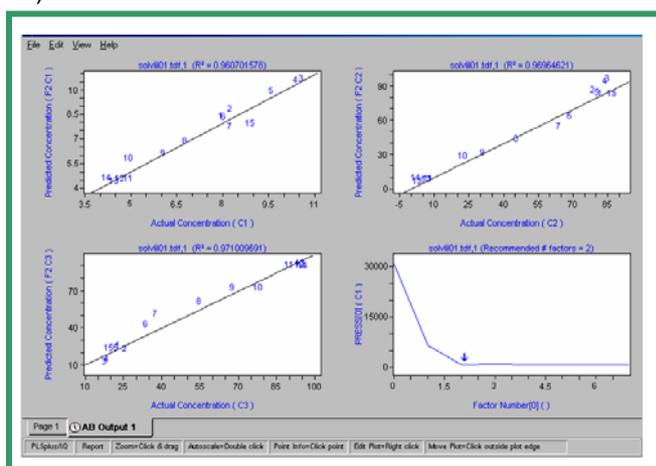
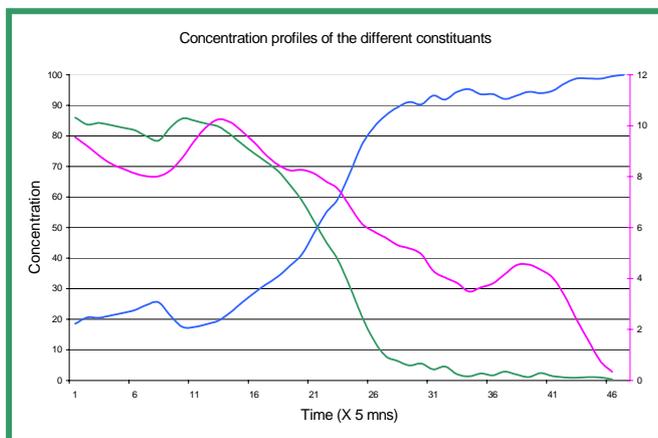


Figure 5 : Cross-validation results

Careful inspection of the data set indicates that the two monomers have different conversion rates. Indeed, the intensity ratio of the bands at 1612cm^{-1} and 1632cm^{-1} attributed to VC_2 and ACM respectively is not constant. This important information is then validated by the concentrations profiles derived from the univariate and multivariate analyses shown in figure 6. Such information that is directly available from the spectra can then assist the chemical engineer in tuning the process and in understanding the properties of the final product.



Subsequently, concentration predictions were performed on spectra of the same reaction that were not part of the training set (Table 2).

The results obtained show good agreement between the predictions and the theoretical values given by the reference method.

We also applied this model to a second reaction run for which the spectrum acquisition time was reduced by a factor 2 (Table 3). The agreement between the predicted and expected values was not quite as good but the order of magnitude of the results still is respectable. In fact, the conditions of the reaction (initiator quantity and temperature) as well as the integration time had been somewhat modified. Certainly when the model is further trained with these conditions, the predictions will be more accurate.

Time interval betw. the reaction start and the spectrum collection	%ACM		%VC ₂		Polymer (arbitraty units)	
	Theor	Pred.	Theor	Pred.	Theor	Pred.
40 mns	8,20	8,16	83,5	80,2	21,3	22,7
1H40	8,64	8,68	74,3	64,8	28,6	30,2
3h20	0,9	1,1	3,8	2,3	91,9	88,6

Table 2

Time interval betw. the reaction start and the spectrum collection	%ACM		%VC ₂		Polymer (arbitraty units)	
	Theor	Pred.	Theor	Pred.	Theor	Pred.
50 mns	10,8	6,6	80,1	88,7	31,2	35,9
1H00	4,83	7,82	76,5	78,8	39,2	25,6
1h45	8,3	7,92	50,9	65,9	40,3	27,8

Table 3

Clearly Raman spectroscopy represents a useful tool to get valuable information - qualitative and quantitative - on polymerisation mechanisms, leading to an optimisation of the manufacturing parameters.

Conclusion

The resulting synergism between Raman spectroscopy and Chemometrics will provide a powerful tool for monitoring and control of manufacturing of polymeric materials.