Real-time Monitoring of Polymerisations in Emulsions by Raman Spectroscopy - Modelling and Chemometrics

Introduction

Real-time monitoring of emulsion polymerization by Raman spectroscopy has been performed. Raman spectroscopy has advantages over other techniques being implemented for process monitoring. It is well-suited for emulsion polymeri-zation reactions because the aqueous solvent does not interfere with the analyte signal by either contributing to the Raman signal or by masking the analyte signal by self-absorption processes. In addition, as it is a scattering phenomenon, the turbidity of an emulsion process is not a severe impediment.

On the other hand there are experimental difficulties arising from the possibility that there is fluorescence emission interfering with the Raman signal, and from the difficulties in extracting signals through windows in reactor walls or in slip streams. In order to avoid these problems a near infrared excitation laser (785 nm) and an immersion probe dipped directly in the reaction medium have been used.

Two parallel ways for data analysis have then been undertaken. The first is based on a mathematical deconvolution of the Raman bands whereas the second relies on more sophisticated multivariate analysis (Chemometrics).

Experimental conditions

The reaction to be followed was a co-polymerization of vinyl dichloride (VC_2) and methyl acrylate (ACM) (90:10). A glass reactor

was especially designed for this feasibility study, enabling the insertion of the Raman probe via the cover of the reactor (fig.1). The pressure was maintained at atmosphere level, and the temperature of the

medium was increased to 32°C. The quantity of initiator had to be adjusted in order to induce the polymerization process and to keep the reaction time acceptable (4-5 hours). The InduRam, a Jobin Yvon on-line Raman analyser, was used for these tests, and includes a fiber-coupled immersion probe. Collection optics on this probe can be adapted to match the optical properties and other physical constraints of the medium.

Principle of the measurements

Polymerization normally proceeds by breaking the carbon double bond of one monomer; the second monomer is then attached via the free electrons. Because these bonds generate very intense Raman bands, one can follow their disappearance as the polymerisation takes place. In summary, the evolution of the reaction can be monitored by following the intensity of the bands associated with the C=C vibrations.

Figure 2: Raman immersion probe

For this example, the estimated reaction time was 5 hours. The automated acquisition and storage of the Raman data was programmed from the LabSpec software. A spectrum was recorded and saved every five minutes. This set of accumulated spectra enabled an analysis, a posteriori, of the reaction.

Preliminary measurements of the pure monomers were necessary to identify their characteristic Raman features (fig.2). Moreover, these spectra are also useful for the subsequent data analysis.
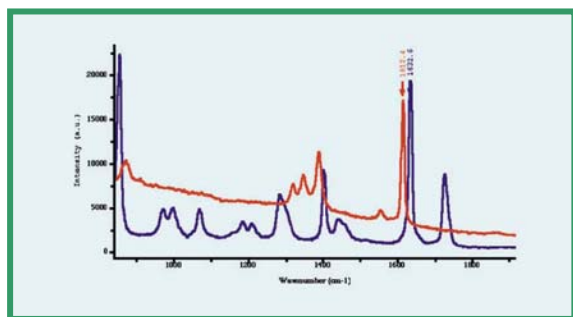
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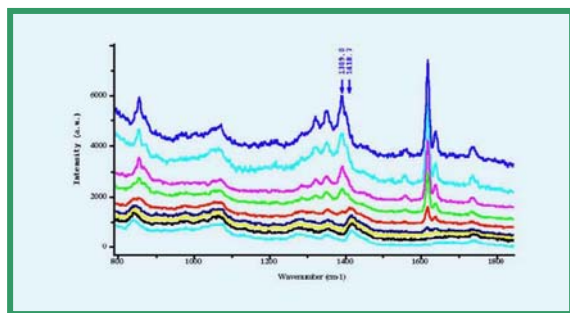*Figure 3: Raman Spectra of the pure monomers (ACM: blue; VC_2 : red)*

The bands associated with the carbon double bonds of VC_2 and ACM located at 1612 and 1632 cm^{-1} respectively are rather well separated. This enables a univariate analysis of the data, in which the intensity of selected Raman bands is monitored.

Figure 4 illustrates the changes in the Raman spectrum during the chemical transformation. The reaction starts slowly but then significantly speeds up; the monomers tend to disappear more and more quickly as the synthesised polymer (broad band at 1410 cm^{-1}) appears. In addition, because the double bonds of the two monomers are distinguishable in the spectra, these results show that the conversion rate of the VC_2 is higher than that of the ACM. Careful inspection of the spectra show the intensity ratio of the bands at 1612 and 1632 cm_{-1} is not constant along the reaction.

Raman data analysis

In order to extract information concerning the progress of the reaction, modelling under LabSpec was done.
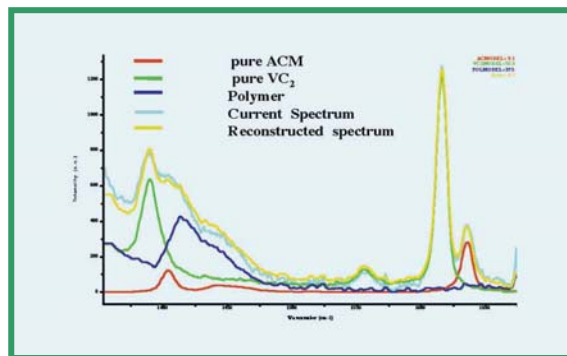
Figure 4: Raman spectra recorded at different stages of the reaction (about every 20 mins)

For this, .model. spectra were selected. These are, on one hand, spectra of the two pure monomers and on the other hand, a spectrum collected at the very end of the reaction, in

which the band associated with the synthesized polymer is clearly visible (fig.5). The deconvolution operation of LabSpec provides a calculation of the contributions of each of these model spectra to the current spectrum. The concentration profiles of the constituents during the reaction are drawn from the quantitative values derived from the deconvolution (fig.6). The mechanisms of the monomer conversions and of the co-polymer synthesis can then be observed, leading to a better understanding of the properties of the final polymer. Figure 6 shows that the beginning of the polymerization itself seems to occur approximately one hour after the addition of the initiator. These profiles also enable one to estimate the time of the transformation process to 3hr 50min and confirm the higher conversion rate of VC_2.

Figure 5. Example of modelling of the current

spectrum from spectra of pure monomers and of the medium at the end of the reaction when mainly the polymer is present.
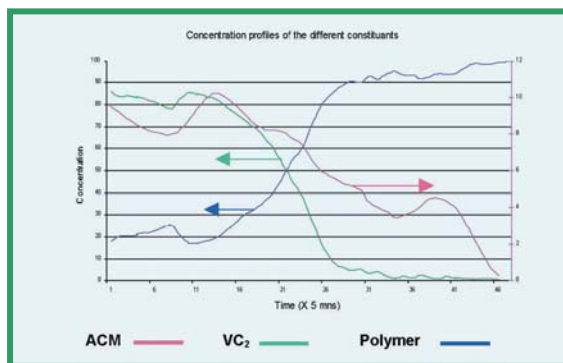

Figure 6. Concentration profiles of the different reaction constituents.

In order to monitor more complex reactions, data analysis based on a multivariate approach (Chemometrics) is expected to be needed. Indeed, when the number of species increases, it is more likely that Raman bands overlap, making the deconvolution method either

impossible or rather inaccurate. The advantage of Chemometrics is that it takes into account a more extended part of the spectrum or even the entire spectrum. It allows one to extract information that may not be accessible at first, when one deals with complex spectra. The PLS_2 algorithm was used for building up the model, that was tested by cross validation (fig.7). The training set consisted of 15 spectra taken at equal intervals during the reaction.
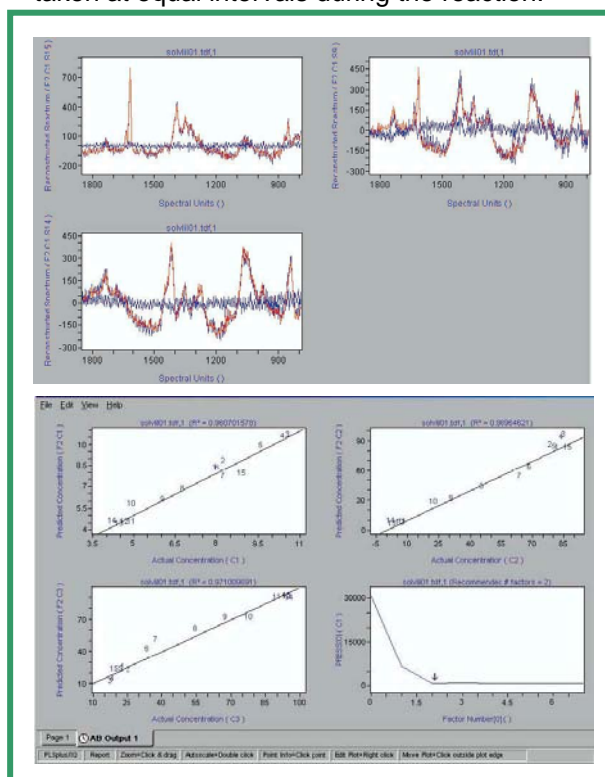

Figure 7. Results from the cross-validation procedure

The model constructed from the training set produced concentration predictions that were made on spectra of the same reaction but that were not part of the training set (tab.1). The results obtained show a good agreement between the predictions and the theoretical values given by the reference method.

The following step was to apply this model to a similar reaction, for which the spectrum acquisition time is reduced by a factor 2 (tab. 2).

The agreement between the predicted and expected values is not as good but the range of the predictions is still acceptable. In fact, part of the discrepancies is due to changes in the reaction conditions (initiator quantity, temperature) as well as collection parameters (integration time). In reality when the model has been trained to account for such changes, it will be much more robust to process variations.

Time interval betw. the reaction start and the spectrum collected	%ACM		%VC2		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 1

Time interval betw. the reaction start and the spectrum collection	%ACM		%VC2		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 2

Conclusion

Raman spectra, in conjunction with Multivariate (Chemometric) Analysis, have been demonstrated to provide real-time information on the progress of a polymerisation reaction. As shown by this example, these results can provide unexpected information on the details of the reaction. in this case, the inequivalent reaction rates of the two monomers. Such information ultimately enables the process engineer to optimise his process.

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