Polymer identification and quantification during continuous on-line processes, by near infrared spectroscopy

S. Montagnier[1] J. Lallemand[2] P. Hebert[1] J. Guilment[1] S. Roussel[2]

[1] Arkema Cerdato, 27470 Serquigny – France, jean.guilment@arkema.com

[2] Ondalys, 4 rue Georges Besse, 34 830 Clapiers, France, sroussel@ondalys.fr

Keywords: Polymerization process, Hierarchical PLS-DA, Discrimination.

1 Introduction

The manufacturing of Ethylene Acrylate copolymers with a third comonomer anhydride can lead to a large number of different products. The variations of comonomers and the polymerization level must be assessed. Models based on near infrared spectroscopy (NIR) provide fast and precise results based on at-line or in-line measurements during continuous processes, when monitoring transitions from one polymer production to another using discrimination models.

The study has been conducted on polymerization processes with transitions from one polymer to another one for a long period of time (several years), to be able to train the models and also get genuine independent test sets in industrial conditions. The main goal was thus to discriminate between the 9 copolymers.

2 Theory

Several discriminant approaches have been compared:

- 1 supervised linear discrimination combined with 3 different discrimination strategies: PLS-DA[1] (Partial-Least-Square Discriminant Analysis) with a (i) direct 9-class approach, (ii) hierarchical discrimination and (iii) “one versus all classes”;
- Another supervised linear discrimination, easier to update if a new class appears: SIMCA (Soft Independent Modelling of Class Analogy)[2]
- 1 supervised non-linear discrimination model: ANN (Artificial Neural Network), for which several approaches have been tested (data compression, layer stize, training algorithms, etc).

The software packages used were OPUS 7.5 software from Bruker, with its PLS QUANT quantitative toolbox and the PLS_Toolbox® from Eigenvector® Research Inc. under Matlab® environment for ANN development, as well as the Deep learning Toolbox from The Mathworks®.

3 Material and methods

Materials: Ethylene Acrylate copolymers with eventually a third co monomer such as an anhydride. The products are made on a continuous process under high pressure and high temperature. The samples are in a pellet form.

Spectroscopy: The spectra are recorded on-line with a Bruker Matrix F instrument equipped with a Q412 probe head, during the whole process with a spectrum about every minute. We use the full

range of the instrument (4000 -12000 cm^{-1}). The resolution is 8 cm^{-1}. Spectra in stable state were used to build the models, and independent spectra, corresponding to the entire transitions, were used to test them.

4 Results and discussion

Different discriminant approaches have been compared: linear models with PLS-DA based on 3 different discrimination strategies (applied in Bruker OPUS software) and non-linear approach with Artificial Neural Networks (ANN with MATLAB deep learning toolbox).

Hierarchical PLS-DA provided a better differentiation for similar classes, but was not able to accurately predict polymer transitions, whereas the "1 versus all" strategy provided less accurate models but able to monitor transition kinetic.

The ANN models were able to provide a one-step discrimination for the 9 classes but required a large number of spectra (~10.000 for calibration, ~6.000 for validation).

The results were tested on an independent test set of ~8.000 spectra.

The best results were very similar with a 1.0% error rate with PLSDA and 0.3% error with ANNs (see below).

Table 1 – Results of classification using PLSDA and ANN

PLSDA : Classification rate = 99%

		True class							
		Family 5b	Family 4	Family 1b	Family 3b	Family 1a	Family 3a	TOTAL	Specificty
Predicted class	Family 5c	0	0	0	0	0	0	0	-
	Family 2	0	0	0	0	0	0	0	-
	Family 5b	475	0	0	0	0	0	475	100%
	Family 4	0	11	0	0	0	3	14	78.6%
	Family 5a	0	0	0	0	0	0	0	-
	Family 1b	0	0	2059	0	0	0	2059	100%
	Family 3b	0	0	0	441	0	77	518	85.1%
	Family 1a	0	0	0	0	3652	0	3652	100%
	Family 3a	0	0	0	0	0	1310	1310	100%
	TOTAL	475	11	2059	441	3652	1390	**8028**	
	Sensitivity	100%	100%	100%	100%	100%	94.2%		

ANN Classification rate = 99.7%

		True class							
		Family 5b	Family 4	Family 1b	Family 3b	Family 1a	Family 3a	TOTAL	Specificty
Predicted class	Family 5c	0	0	0	0	11	0	11	-
	Family 2	0	0	0	0	0	0	0	-
	Family 5b	475	0	0	0	0	0	475	100%
	Family 4	0	4	0	0	0	3	7	57.1%
	Family 5a	0	0	0	0	0	0	0	-
	Family 1b	0	0	2059	0	0	0	2059	100%
	Family 3b	0	0	0	441	0	0	441	100%
	Family 1a	0	6	0	0	3640	0	3646	99.8%
	Family 3a	0	1	0	0	1	1387	1389	99.9%
	TOTAL	475	11	2059	441	3652	1390	**8028**	
	Sensitivity	100%	36.4%	100%	100%	100%	99.8%		

5 Conclusion

This study allowed developing a discriminant strategy for on-line polymer identification during transition phases, with NIR.

The importance of the chemometrics' method choice has been illustrated. It strongly depends on data, discrimination difficulty, the application, and the objectives pursued.

The total goal, which corresponds to the quantification of acrylate content and MFI control for the stable phases of the process and the following of the transitions, can be achieved using a multi-level approach with linear methods based on PLS.

We expect to be able to tackle the entire problem with a nonlinear approach using multi-level ANN.

6 References

[1] M. Barker, W. Rayens. Partial Least Squares for Discrimination. *Journal of Chemometrics*, **200**3, 17(3), 166-173.

[2] S. Wold, and M. Sjostrom. SIMCA: A Method for Analyzing Chemical Data in Terms of Similarity and Analogy - (Chapter Book). Chemometrics: Theory and Application. 1977. 52: 243–282