



Universidade do Minho  
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### IN-LINE CHARACTERIZATION OF PP/CLAY NANOCOMPOSITES PREPARATION BY NIR SPECTROSCOPY

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#### KEYWORDS

Near-infrared spectroscopy; nanocomposites.

#### ABSTRACT

The performance of polymer/clay nanocomposites depends on the clay dispersion levels in the matrix. This work uses on-line Near-Infrared (NIR) spectroscopy to monitor the evolution of mixing upon the preparation of polypropylene/clay nanocomposites by melt compounding. The corresponding chemometric model uses parameters derived from rheology and FT-IR and data provided by the compounding equipment. The method is successfully applied in real-time conditions.

#### INTRODUCTION

Polymer-clay nanocomposites have found wide practical application, due to their good performance even at low clay loadings. Nevertheless, the production of these compounds continues to face difficulties in establishing clear correlations between processing conditions and mixing quality. Therefore, the availability of fast-responsive on-line techniques continues to be of great practical interest.

In recent years, NIR spectroscopy became a routinely used tool for monitoring and control purposes in the industrial scene (Blanco and Villarroya 2002). However, the use of NIR for on-line monitoring of the preparation of polymer/clay nanocomposites is still limited (Moghaddam *et al* 2009; Witshnigg *et al* 2010). This work uses on-line NIR to monitor the evolution of mixing upon the preparation of polymer nanocomposites by melt compounding. The method is successfully applied in the prediction of the dispersion level of PP matrix nanocomposites during mixing time.

#### EXPERIMENTAL

Nanocomposites based on polypropylene (PP, Moplen HP500N, Lyondell-Basell) and a nanosilicate (Cloisite

20A, Southern Clay Products) were prepared in a batch mixer Haake Rheomix OS600 (Thermo Scientific Inc.), at 200 °C during 7 minutes, using different rotor speeds (50, 100, 150, 200 rpm). The PP matrix was compatibilized with Maleic Anhydride modified PP (PP-g-MA, Polybond 3200, Crompton). The samples of PP/PP-g-MA/C20A have (90/5/5)% in weight respectively.

A threaded hole was machined in the front plate of the mixing chamber of the batch mixer to accommodate the NIR probe. The spectra were measured with a resolution of 8 cm<sup>-1</sup> and accumulation of 4 scans (less than 2 seconds per spectrum).

#### CHEMOMETRIC MODEL

NIR spectra are complex and influenced by a number of physical, chemical and structural variables. Thus, NIR spectroscopy uses chemometrics to relate spectral data with other properties (Blanco and Villarroya 2002). A major step in this process is the definition of the calibration parameters, to be obtained by reference techniques. In the case of nanocomposites, they should characterize the degree of clay dispersion. In this study the chemometric model comprises a normalized average of 7 parameters (defining the clay dispersion degree in a 0 – 100% scale), derived from:

- Rheology – storage and loss moduli (Cassagnau 2008), melt yield stress (Lertwimolnum and Vergnes 2005) and power law index (Durmus *et al* 2007).
- FTIR – wavenumber shift of the in-plane and out-of-plane Si-O peaks (Cole 2008).
- Thermomechanical data (torque) from the mixing equipment (Lertwimolnum and Vergnes 2005).

The quality of the chemometric model is assessed by its Coefficient of Determination,  $R^2$  (values above 95% are preferred), the root mean error of estimation (RMSEE), that should be as small as possible, and the Residual Prediction Deviation (RPD), which should be above 8 (Adams 1995).



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### RESULTS

Figure 1 shows the calibration line and quality parameters of the chemometric model, confirming this as a statistically reliable model for the assessment of the clay level of dispersion.

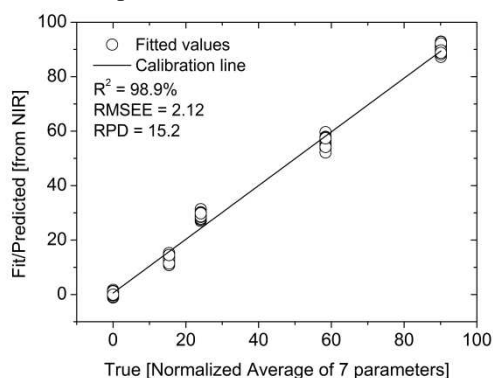


Figure 1: Chemometric Model.

The model was applied in real-time conditions, for monitoring the evolution of the dispersion state of two new samples, prepared with 125 and 175 rpm. Figure 2 presents the torque curves from the Haake Rheomix and the predicted values of the degree of dispersion.

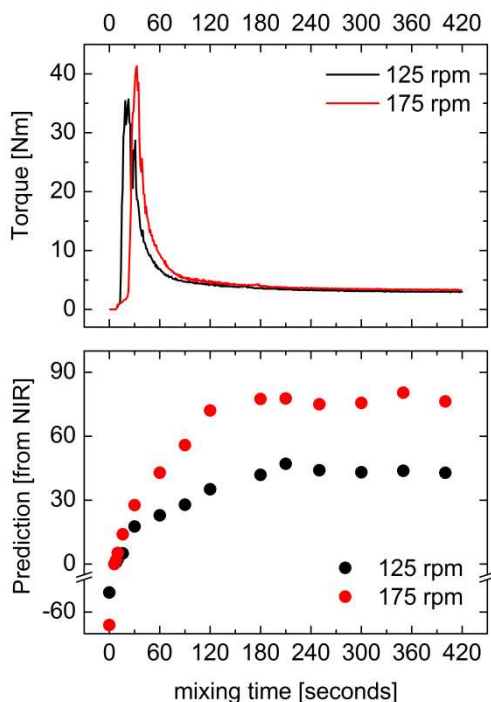


Figure 2: On top Torque vs time curves from the Haake Rheomix and on the bottom the NIR prediction results.

The predicted values for  $t=0$  seconds are very low due to the low signal of these spectra. Upon mixing the predicted values of the dispersion state show an increasing trend during the initial phase but tend to stabilize after a certain time. However, for the sample prepared at 125 rpm this stabilization occurs later ( $\pm 180$  seconds) than for the sample prepared at 175 rpm ( $\pm 120$  seconds). These results show that the final mixing state of the prepared nanocomposite is reached earlier with increasing rotor speed. Furthermore, the final dispersion degrees predicted by NIR are of  $\pm 42\%$  for 125 rpm and  $\pm 78\%$  for 175 rpm, which are in agreement with the reference values measured for the calibration samples prepared at 100 (24.1%), 150 (58.4%) and 200 (90.1%) rpm. Overall, these results confirm that the dispersion quality, of PP matrix nanocomposites, increases with increasing rotor speed.

### CONCLUSIONS

The possibility of using on-line NIR to characterize the evolution of dispersion during the preparation of nanocomposites by melt compounding was demonstrated.

The chemometric model was successfully applied in the assessment of the clay dispersion in a PP matrix nanocomposite in real-time conditions.

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**JOANA M. BARBAS** was born in Porto, Portugal. In 2003 got her degree in Chemistry by University of Minho. In 2007 concluded a post-graduation also from U. Minho. From 2004 to 2008 worked in PIEP on industry related R&D. Since October 2008 is a PhD student at the IPC/I3N in University of Minho.