ON-LINE CHARACTERIZATION OF NANOCOMPOSITES PREPARATION BY NEAR-INFRARED SPECTROSCOPY

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KEYWORDS

Near-infrared spectroscopy; rheology; nanocomposites

ABSTRACT

Growing demands on the quality of polymeric products, as well as reduction of costs in production and processing requires the development of innovative, more reliable and faster control methods. Thus, on-line monitoring became a very important research topic. In recent years, near-infrared (NIR) spectroscopy has become an analytical tool frequently used in many chemical production processes but its application to monitor on-line nanocomposites preparation is still limited. The use of NIR spectroscopy combined with chemometric models is a time consuming process. Therefore, the present work aims to develop appropriate and reliable methodologies to monitor nanocomposites preparation by NIR spectroscopy.

INTRODUCTION

Properties of polymeric nanocomposites are strongly dependent on their morphology. Therefore, it is important to monitor the morphology development during production. NIR spectroscopy is already routinely used in polymer industry (Hansen and Vedula 1998; Vedula and Hansen 1998), but its application to monitor on-line nanocomposites preparation is yet to be explored in a more detailed way (Laske et al 2009).

The use of fiber optics probes connected to a NIR Spectrophotometer could be a powerful technique to follow-up the morphology evolution during the nanocomposites preparation by melt mixing in a modular co-rotating twin-screw extruder (TSE).

The present work aims to develop a rather quick, reliable and robust method to monitor nanocomposites preparation using NIR spectroscopy, based on rheological parameters.

EXPERIMENTAL PROCEDURE

Nanocomposites based on polypropylene (PP) and nylon-6 (PA6) matrices and an organo-layered nanosilicate were prepared in a TSE Leistritz LSM 30.34 under different screw speeds of 50, 100, 200 and 300 rpm, using a 3 kg/h throughput and the barrel temperature was set at 200 ºC and 240 ºC for PP and PA6 nanocomposites respectively. The nanoclay dispersion at a given position of the extruder barrel (see Figure 1) was monitored by on-line NIR.

The on-line monitoring was carried out by a NIR spectrophotometer Matrix F (Bruker Optics), the NIR spectra analysis and chemometric model developments were done using OPUS® Quant2 software (*Bruker Optics*).
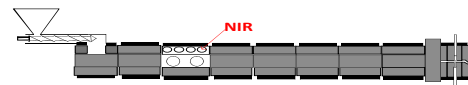

Figure 1: Extruder barrel configuration and NIR probe location

For off-line rheological characterization of the samples collected at the same barrel position an oscillatory rheometer ARG2 (TA Instruments) was used; measurements were performed using parallel plate geometry and a frequency sweep of 0.1-100 rad/s at a constant strain within the linear regime for each material, for PP matrix the temperature set was 200 ºC and for PA6 matrix 240 ºC. The results obtained were fitted using a modified Carreau-Yasuda model in Equation (1) (Lertwimolnun and Vergnes 2005) where σ_0 (yield stress) is the parameter of interest, and allometric power-law as Equation (2), where b is the parameter used (Durmus et al 2007). The fitting was done with OriginPro 8 software.

$$\eta^*(\omega) = \frac{\sigma_0}{\omega} + \eta_0 * \left[1 + (\lambda * \omega)^a\right]^{\frac{n-1}{a}} \tag{1}$$

$$\eta^*(\omega) = A\omega^b \tag{2}$$

RESULTS

The rheological curves exhibit different behaviors of the nanocomposites according to the processing conditions used and the polymer matrix. Examples of rheological curves and respective fittings are shown in Figure 2, and all rheological parameters considered for the development of the chemometric model are summarized in Tables 1 and 2. Only fittings with $R^2 > 95\%$ were considered. In the case of PA6 matrix the shape of the rheological curves does not allow the fitting with Carreau-Yasuda model (Figure 2 (a)), therefore only parameter b and G' values were used for in the chemometric model.

Table 1: Rheological parameters obtained from fitting for PP matrix nanocomposites

Parameters	G'	σ_0	b
PP+5%PPgMA	7.51E+01	0	-0.267
D67G 3-50	1.16E+03	1363	-0.774
D67G 3-100	2.49E+03	2773	-0.832
D67G 3-200	4.17E+03	2850	-0.863
D67G 3-300	4.18E+03	4526	-0.859

Table 2: Rheological parameters obtained from fitting for PA6 matrix nanocomposites

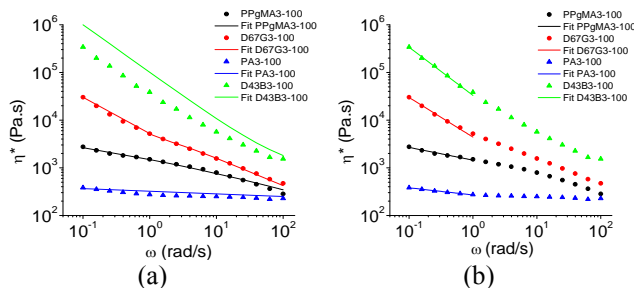| Parameters	G'	σ_0	b
PA	2.40E+00		-0.121
D43B 3-50	6.08E+03	No adjustable fitting was found	-1.232
D43B 3-100	3.90E+04		-1.033
D43B 3-200	4.53E+04		-1.115
D43B 3-300	2.30E+03		-1.271

Figure 2: Example of frequency sweep curves and respective Carreau-Yasuda fitting (a) and allometric power-law fitting (b).

For the NIR chemometric model development a few samples were left aside as independent samples. This sample group will allow the final validation of the developed model. Calibration model and final validation results are presented in Tables 3 and 4 respectively.

Table 3: Results of the Calibration Model developed with different parameters.

		R^2	Mean Error of Estimation	RPD
PP	G'	99.34	0.143	12.3
	σ_0	97.06	0.281	5.83
	b	99.95	0.006	45.6
PA6	G'	98.43	0.918	7.98
	b	97.16	0.045	5.93

Table 4: Results of the final validation of the chemometric model developed with different parameters.

		R^2	Mean Error of Prediction	Bias
PP	G'	96.63	0.317	0.0318
	σ_0	96.65	0.339	-0.0011
	b	99.06	0.028	0.0055
PA6	G'	18.56	6.38	-0.0176
	b	94.49	0.0621	-0.0021

CONCLUSIONS

G' and σ_0 are good distinction parameters, although their use is not universal. Assuming that an increase of the *b* value means better nanoclay dispersion, this indicates that the chemometric model developed is valid and able to discriminate taking into account the shear thinning value. Using appropriate parameters, NIR spectroscopy is an apt and powerful tool for on-line monitoring of nanocomposites production.

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JOANA M. BARBAS was born in Porto, Portugal. In 2003 got her degree in Chemistry by University of Minho, with final work thesis on *Reactive Extrusion of Thermoplastic Vulcanizates*. In 2007 concluded a post-graduation in Materials Processing and Characterization, also from U. Minho. From 2004 to 2008 worked on PIEP on industrial R&D. Since October 2008 is a PhD student at the Polymer Engineering Department at University of Minho.