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Multivariate near infrared spectroscopy models to monitor polycondensation production process reactions

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The control of polycondensation progress in the reactor is usually carried out by the determination of the acid value and the Average Molecular Weight (AMW) using analytical methods that are expensive and time consuming. Alternatively, this work reports the use of near infrared spectroscopy (NIRS), coupled with multivariate calibration techniques, to determine these two parameters. Thus, polycondensations of Adipic Acid with 1,6-Hexanediol were carried out at 130 °C and followed in-line using NIRS. Principal Component Analysis (PCA) was used to perform the qualitative analysis of the spectra, whereas Partial Least Squares (PLS) regression was used to develop calibration models between the spectra and the acid value and the average molecular weight of the polymers. The results support that NIRS, in combination with multivariate calibration, is a promising and an accurate method for monitoring the polycondensation process.

1. Introduction

Polycondensation of dicarboxylic acids with diols is usually monitored by off-line titrimetric determinations of acid and hydroxyl values, and by off-line determination of molecular weight distribution (MWD), through size exclusion chromatography (SEC) [1,2]. However, these conventional off-line monitoring methods have many limitations because they are expensive, time consuming and present large errors. Moreover, to follow the reactions it is required to withdraw and analyze a considerable number of samples from the reaction mixture. Due to these drawbacks, the off-line analytical methods become unsuitable for an accurate reaction monitoring and Near-infrared spectroscopy (NIRS) appear as a cheaper, faster and accurate alternative to surpass the limitations of conventional off-line monitoring methods.

NIRS is a well-established analytical technique based on the absorption of electromagnetic energy in the region from 780 nm to 2500 nm (12,820–4000 cm^{-1}). It allows multi-component analysis in a fast and non-destructive way, without requiring complex pre-treatments. In the NIR region, a component typically absorbs at more than one wavelength and the absorbance at a given wavelength may have contributions from more than one analyte [3]. Moreover, NIRS affords the simultaneous prediction of physical and chemical parameters from a single spectrum. Another important advantage of NIR spectroscopy is the possibility of using it directly in-line with fiber-optic probes, which makes it suitable for process control purposes. Actually, the use of fiber-optic probes immersed in a reaction medium and connected to the spectrometer, opens up new perspectives for process control in polymerization.

Although, due to considerable overlap of the absorption bands in NIR spectral region, it requires the use of

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multivariate regression techniques, to develop effective calibration models. In this work, Principal Components Analysis (PCA) was used to perform the qualitative analysis of the data, whereas a Partial Least Squares (PLS) was applied to derive the model that relates the NIR spectra with the acid value and the Average Molecular Weight (AMW), during polycondensation [3]. The correlation between the absorption of NIR radiation and the analytical values, obtained using the reference methods, can be improved through the use of specific spectra pre-processing and variable selection methods. Pre-processing of the spectra reduces variations that are not directly related to the analyte concentration, such as random noise, baseline drift, and light scattering [3,4].

The application of NIR spectroscopy to determine the main analytical properties during polycondensation is reported in the literature [5–9], but few have used an in-line fiber-optic probe. Robbins et al. [5] determined, using NIR spectroscopy at 1415 nm and applying univariate linear regression, the average molecular weight based on the disappearance of the hydroxyl group. Likewise, Lee et al. [6], using univariate linear regression, related the hydroxyl value with the second derivative of the NIR spectra. Blanco et al. [7] developed multivariate models for different stages of the production process. On the other hand, Marengo et al. [8] developed a model for hydroxyl and acid values using artificial neural networks and compared it with conventional calibration approaches. Heikka et al. [9] developed a predictive calibration model based on Barry Wise's non-linear PLS for the acid value in the polycondensation of different combinations of two dicarboxylic acids and six diols, using an in-line reflectance NIR probe. Also, calibration models for acid and hydroxyl values, as well as water content have been developed.

In this study, Principal Component Analysis (PCA) identifies the decrease of the acid value, the increase of AMW and the esterification and vacuum steps of the polycondensation. Moreover, this work presents the development of calibration models between analytical and spectral data for the acid value and the average molecular weight during the polycondensation reaction, thus allowing the use of NIRS as a fast and cheaper method to control polymerization reactions.

2. Experimental

2.1. Materials

Adipic Acid (⩾99.6%), 1,6-Hexanediol (99%) and Bismuth (III) Trifluoromethanesulfonate (99%) were obtained from Sigma–Aldrich. Other chemicals and solvents were used as received from commercial sources without further purification.

2.2. Polycondensation

The polyesters were synthesized in accordance with the classical two-step polycondensation reaction. In the first one, the esterification proceeds under dry nitrogen atmosphere and the water formed is separated by distillation, until an elevated percentage of the initial acid has reacted. As the reaction proceeds, the viscosity of the reacting medium increases hindering the water removal. Thus, at later stages of reaction, it was required to apply vacuum not only to remove the volatile water but also the unreacted diol.

The polyesters were produced by direct esterification of Adipic Acid (1.23 mol, 145.39 g) and 1,6-Hexanediol (1.12 mol, 163.46 g), in a 500 mL four-necked glass reaction vessel equipped with stirring, temperature control and a water trap, under dry nitrogen atmosphere. A NIR transflectance fiber-optic probe was immersed in the reaction medium.

Bismuth Triflate was used as catalyst (0.3 mmol, 0.19 g). Esterification was carried out at 130 °C, during several hours at atmospheric pressure. After the pre-established reaction time (≈6–8 h), vacuum was gradually applied during the esterification (10 mbar). Samples were withdrawn from the reaction vessel during the polycondensation. The measurement of acid value via titration was used to determine the conversion of the reaction.

Mechanical stirring was used, instead of magnetic agitation, in one of the polymerization reactions.

2.3. Analyzes

A Near Infrared System FT-NIR Perkin–Elmer Frontier spectrophotometer, equipped with a transflectance fiber-optic probe, with a path length of 5 mm was used to collect the NIR spectra in line and in situ. Spectral measurements were made at 2 cm^{-1} intervals over the wavenumber range 4000–10,000 cm^{-1}. Each spectrum was obtained from the average of 30 scans, with a spectral resolution of 32 cm^{-1}.

The acid value was determined according to the standard titrimetric method ASTM D-465-01 described elsewhere [10]. The Average Molecular Weight (AMW) was determined by SEC measurements [11].

An apparatus of Waters SEC Instrument equipped with a refractive index detector Waters 2414 was used. A combination of four PLgel MIXED columns from Agilent (50 and 100 Å) was used with THF as eluent (flow rate 1.0 mL min^{-1}). Commercial polystyrene standards were used for calibration. Since polystyrene-calibrated SEC measurements overestimate the real molecular weights of aliphatic polyesters [12], a factor of 0.55 was applied to the measured AMW. This factor was determined by the correlation of SEC measurements with high-performance gel permeation chromatography (HPSEC, Viskotek TDAmax; with: a differential viscometer, right and low laser-light scattering, and refractive-index detectors).

2.4. Data analysis and calibration development

All calculations were carried out using Matlab version 7.9 (MathWorks, Natick, MA) and the PLS Toolbox version 4.0 (Eigenvector Research Inc. – USA) for Matlab. Only de region between 9000 and 4500 cm^{-1} was used for calibration because the noisy (<4500 cm^{-1}) and non-informative (>9000 cm^{-1}) ranges oft he spectra were excluded.

As mentioned above, data analysis was performed using PCA for a qualitative analysis of the spectra, whereas the