

IN-SITU REAL-TIME MONITORING OF PARTICLE SIZE AND POLYMER AND MONOMER CONTENTS IN EMULSION POLYMERIZATION PROCESSES USING NEAR INFRARED SPECTROSCOPY

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Summary

This work reports results of in-situ real-time monitoring of emulsion polymerization processes using near infrared spectroscopy (NIRS). Besides the monitoring of the monomer and polymer content, the results show that reasonable estimates for the average particle size of the growing polymer particles present in the reaction medium can be inferred from the spectra. This is possible because the presence of particles affects the spectra (through scattering, diffraction, and other mechanisms). Thus, by using appropriate calibration and decoupling the effects of polymer content and particle size, it is possible to obtain reliable calibration models for particle size, in addition to the monitoring of monomer and polymer concentrations.

Keywords

On line monitoring, emulsion polymerization, methyl methacrylate, particle size, near infrared spectroscopy.

Introduction

Emulsion polymerization processes are largely used for industrial production of water-based polymers for the manufacturing of paints, resins, adhesives, paper coatings, etc. Besides the environmentally friendly features due to the use of water instead of solvents as dispersing medium, these processes are very versatile for producing emulsion polymers with distinct properties and applications. Emulsion polymers are “products by processes”, in the sense that the major properties are defined by the conditions of the synthesis [1]. Thus, the process monitoring is of crucial importance to the control of the product quality.

Among the different techniques available for on-line monitoring of polymerization processes [2,3,4,5,6], vibrational spectroscopic techniques, such as near-infrared spectroscopy (NIRS), combined with the use of optical fibers, present special advantages, namely, the possibility of remote, in-situ, real-time, and multipurpose monitoring of the different variables using the same instrument.

Some previous works have shown the potential of this technique for monitoring of emulsion polymerization processes. In special, the possibility of monitoring the particle size, in addition to the monomer and polymer contents has been reported by some authors [7,8,9,10, 11, 12]. This feature of monitoring the particle size is of special importance for heterogeneous polymerization processes because particle size is extremely useful information: particle size affects some important end-use

properties of the product and particle size affects the kinetics of emulsion polymerization processes.

The aim of the present work is the study of NIRS for in-situ, real-time monitoring of the monomer and polymer concentrations and the average size of the polymer particles, during the semi-batch process of emulsion polymerization of methyl methacrylate (MMA).

Methodology

In order to decouple the variations of particle size and polymer content, the reactions were carried out in a semi-batch mode, some of them unseeded, and most of them seeded using the particles formed in the previous run. In this way, it is possible to have particles of increased size from one run to the next one, while the polymer concentration is kept on a given range.

Reactions were carried out in a 3 L laboratory scale stainless steel reactor (BüchiGlassUster) with automatic control of temperature, feeding flow rates and stirrer speed. Samples of the reactor content were periodically taken from the reactor to measure the polymer and monomer contents by gravimetry, and the average particle size by dynamic light scattering/photon correlation spectroscopy (Coulter N4 Plus). Near infrared spectra were measured in-situ by an immersion probe (Hellma 661.622-NIR, transmittance mode, optical path 1 mm) and a NIR spectrometer (Bruker IFS-28N).

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Calibration models for monomer and polymer contents and for particle size were obtained by using conventional PLS (partial least squares) regression. The number of latent variables for each calibration model was determined by leave-one-out cross validation. In addition to cross validation, a sub-set of the data gathered, not used in the calibration step, was used to test the capability of the developed calibration models to represent new data.

Results

It is particularly interesting to investigate the effect of the presence of particles on the NIR spectra. Figure 1(a) and (b) shows the spectra obtained for water and MMA monomer. The characteristic bands of water (in blue) at wavenumbers 5250 and 7000 cm^{-1} (corresponding to OH bonds) and of MMA (in red) at 4000-4800 cm^{-1} and 5500-6200 cm^{-1} (corresponding to $\text{H}_2\text{C}=\text{C}$) can be seen. Figure 1(c) shows a typical spectrum colleted during an emulsion polymerization run, in which polymer particles are present along with water and some unreacted monomer. Besides the characteristic bands for water and MMA, a strong signal can be observed in the region 10500-13000 cm^{-1} . This band is the result of the presence of particles in the medium. It is clear that the particles affect the NIR spectra. Thus, the spectra provides information about the particles, and by calibration, NIRS can be used to monitor particle size along with monomer and polymer contents.

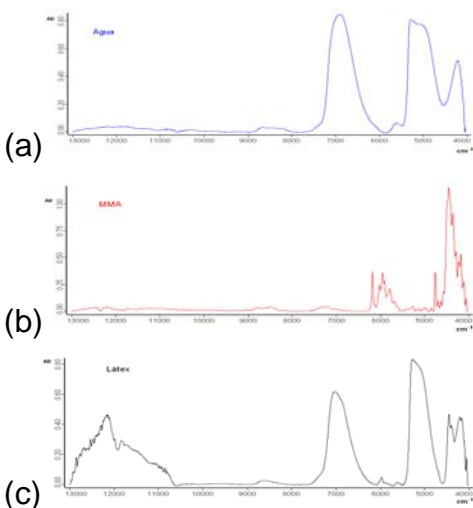


Figure 1. NIR spectra of (a) water, (b) MMA and (c) emulsion (water, monomer and polymer particles).

Figure 2 shows the comparison of the variables monitored from NIR spectra and calibration models with the reference off-line measurements. Consecutive batches are plotted in sequence in this figure. The last part of the plot corresponds to the measurements not used in the calibration step, so this part of the plot is a true external validation. It is noteworthy the ability of the calibration models to follow the trends of the experimental data quite well, within the expected typical variability of the data.

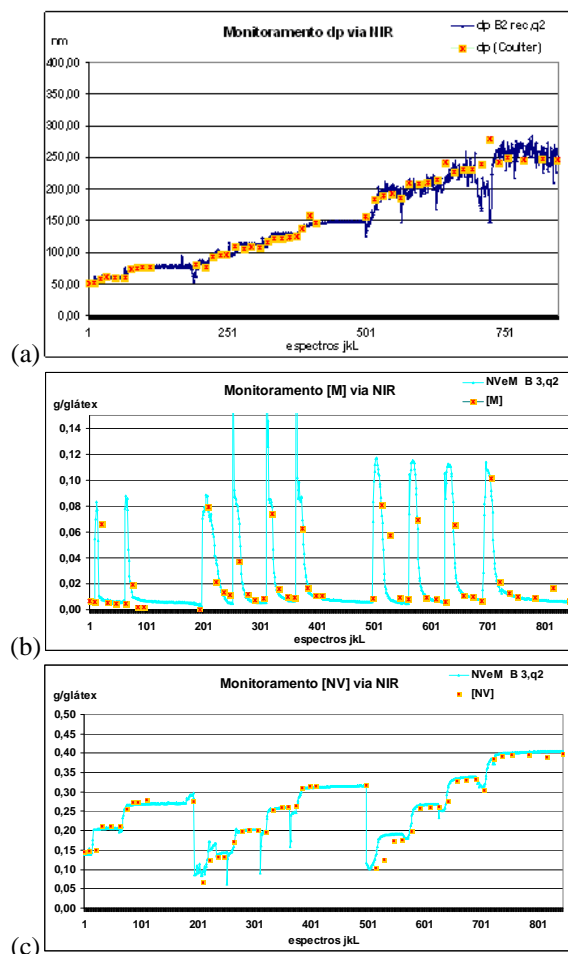


Figure 2 – Comparison between the estimates from the spectra measured in-line and the calibration models (blue curves) and the off-line measurements (yellow symbols), for (a) particle size, (b) residual monomer, and (c) polymer content.

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