Near infrared spectroscopy is widely used for determination of polymer properties through in line and real time monitoring of reaction systems. Experimental runs were performed to evaluate the capacity of the NIRS technique to monitor VAc/AA copolymerizations carried out in suspension reactors. It was shown that NIRS technique can be successfully used to monitor VAc/AA suspension copolymerizations and that very good calibration model can be developed, describing very well the concentration of reactive constituents inside the reactor system. The obtained calibration and validation results indicate that NIRS can be employed for suspension processes intended for process monitoring and control of copolymer composition in VAc/AA copolymerizations performed in suspension reactors.

**Keywords:** Acrylic Acid, Vinyl Acetate, Batch Suspension Copolymerization, Near Infrared Spectroscopy.

**Monitoramento de Copolimerizações em Batelada de VAc/AA Usando NIRS**

Espectroscopia no Infravermelho próximo é largamente utilizada para determinação de propriedades poliméricas através do monitoramento em linha e em tempo real de sistemas de reação. Vários experimentos foram conduzidos para avaliação da capacidade da técnica NIRS em monitorar copolimerizações de VAc/AA em processos de polimerização em suspensão. Mostrou-se que a técnica NIRS pode ser utilizada com sucesso para o monitoramento de copolimerizações em suspensão de VAc/AA e que bons modelos de calibração podem ser desenvolvidos, descresendo de forma satisfatória a concentração dos constituintes da reação dentro do reator. Os resultados obtidos para calibração e validação indicaram que o NIRS pode ser empregado em processos em suspensão visando o monitoramento e controle da composição do copolímero de VAc/AA em copolimerizações conduzidas em processos em suspensão.

**Palavras-chave:** Ácido Acrílico, Acetato de Vinila, Copolimerização em Suspensão, Espectroscopia no Infravermelho Próximo.

**Introduction**

In systems with different reactive species, measurement of the end-use polymer properties may depend on the copolymer composition. The relation between the operation reaction conditions and the monomer conversion typically requires the use of an accurate polymerization model to predict the composition of the polymer as a function of monomer consumption, or the implementation of additional in line sensors for determining the conversion of each species and / or the composition of the copolymer. In addition, in some cases robust analytical instrumentation and sensors necessary to provide in line measurements of molecular properties (such as copolymer composition and molecular weight distributions, degree of branching, etc.) are not available or require excessive time to perform the measurements, which often are not very reliable.

Near infrared spectroscopy (NIRS) is extensively used for investigation of polymer quality through in line and off line measurements of structural and kinetic data of polymeric systems. NIRS is a powerful tool that allows for measurement of many polymer properties, such as average particle
size, monomer conversion, chemical compositions, and average molar mass in several polymerization systems (e.g. suspension, emulsion, bulk, solution, etc).\[^{[11-12]}\] Normally, spectroscopy measurements of the reaction medium can be correlated with a property of interest.

NIRS technique is generally employed in suspension polymerization processes for monitoring and/or control of average particle size and other morphological properties of interest.\[^{[13-16]}\] In the particular case of suspension polymerization process, process monitoring is possible due to distinct phenomena, such as reflection, refraction and random scattering on the surface of the polymer particles. The large scattering / absorption ratio, usually regarded as a disadvantage for spectroscopy applications, plays a important role for analysis of the morphological features of polymer particles obtained in suspension polymerization systems.\[^{[7]}\]

Regarding the use of NIR spectroscopy intended for monitoring and control in suspension polymerization systems, it is very important to emphasize the pioneering studies developed by Santos et al.\[^{[13, 14]}\]. According to these authors, it is possible to monitor and control the average particle size during styrene suspension polymerizations in real time using the NIRS technique associated to manipulation of some of the process variables (for instance, the agitation speed). Additional applications of NIRS in simultaneous semibatch suspension/emulsion process include the detection of core-shell structures.\[^{[17]}\] More recently, de Faria Jr. et al.\[^{[15, 16]}\] showed that NIRS technique can be successfully used for in-line and in situ prediction of important morphological properties of PVC particles, such as bulk density (BD), cold plasticizer absorption (CPA) and average particle diameter (Dp).

In suspension polymerization process it is very difficult to find good calibration models for monomer conversion due to variations of the spectral signal largely dominated by scattering phenomena.\[^{[13, 14]}\] In the present work, it will be shown for the first time that NIRS can be successfully used to monitor the polymer composition in copolymerizations of VAc/AA performed in suspension process. The main advantage of VAc/AA suspension process arises from the partition of AA between the aqueous and the organic phases, which makes the scattering signal to be less important that the absorption AA signal obtained in the aqueous phase. As a consequence, very good partial least squares (PLS) calibration models can be obtained for the AA aqueous concentration. With the information of the AA concentration provided by the NIRS, a phenomenological copolymerization model can be used as reference for computation of the concentrations of the reactive species in both aqueous and organic phases during the reaction and for optimization of monomer feed and temperature profiles.\[^{[18-20]}\]
Experimental Procedure

Poly(vinyl alcohol) (PVA), used as suspending agent with a degree of hydrolysis of 85% and the initiator benzoyl peroxide (BPO) with a minimum purity of 98% were supplied by VETEC Química Fina, (Rio de Janeiro, Brazil). Nitrogen was supplied by AGA S. A. (Rio de Janeiro, Brazil) with 99.9% purity. Monomers acrylic acid and vinyl acetate were supplied by Tedia Brasil (Rio de Janeiro, Brazil), with a minimum purity of 99.9%. Distilled water was used as the suspending medium. Unless otherwise stated, chemicals were used as received, without additional purification.

VAc/AA Copolymerization reactions were performed in a 1-L jacketed glass reactor (FGG Equipamentos Científicos Ltda, São Paulo, Brazil) with a total organic load of 30 wt % under inert atmosphere. Nitrogen was used to maintain the reaction environment free of oxygen. Initially, the reactor was fed with distilled water, containing the specified amount of suspending agent (approximately 0.1 wt % of PVA, related to the amount of water). When the desired temperature of 70 °C was achieved, the reagents and the initiator (approximately 0.8 wt % of BPO, related to the organic phase content) were added. The system was kept with a constant and vigorous agitation of 1000 rpm under isothermal conditions. The experimental setup used to carry out the copolymerization reactions was similar to the one described by Machado et al. [18], and the reader is referred to this publication for a more detailed description of reactor apparatus and analytical analysis.

In situ near infrared spectroscopy measurements of the reaction medium were carried out using a NIR spectrophotometer (Monochromator model 6500-On line supplied by NIRSystems, Inc., USA) equipped with a stainless steel interactance probe with dimensions of 30 cm length and diameter of 1.905 cm with 3 mm path length. A 3 m long fiber optic cable was used for light transmission. At each sampling time, 32 scan spectra were collected automatically with intervals of one minute and average spectra were recorded and used for analysis. This instrument has a wavelength range of 400 to 2500 nm, which comprises both the visible and the near infrared spectra of the samples. The NSAS® (Near Infrared Spectral Analysis System) software was used for data acquisition and spectral data treatment.[21]

Results e Discussion

Figure 1 shows typical profiles of temperature and conversion during VAc / AA copolymerizations. As can be observed, the reaction presents remarkable nonlinear features, such as maximum conversion limit and strong autoacceleration, induced by the increase of the system viscosity during the batch copolymerization reactions, which characterize the well-known glass and gel effects. Figure 1 also illustrates that, during the autoacceleration period, reaction temperatures may increase.
because of the significantly high rates of heat generation, leading to the increase of approximately 3°C in the average reaction temperature.

According to Machado et al.\textsuperscript{[18]} during VAc/AA copolymerizations monomer conversion profiles can be divided into three main characteristic stages: (1) The first stage, which takes approximately 50 min, is characterized by the preferential consumption of the most reactive monomer (AA). The monomers are consumed up to conversion values that are similar to the initial AA amount. (2) The second reaction stage also takes approximately 50 min of reaction, being characterized by a strong acceleration of the reaction, with the preferential polymerization of VAc. During this stage, there is no significant amount of the AA monomer in the organic phase. (3) The third stage is characterized by the limitation of monomer conversion, probably due to the diffusion limitations caused by the increase of the viscosity of the reaction medium.

It is very important to emphasize that both glass and gel effect take place during all stages of the copolymerization reaction, representing a combined effect on the polymerizations. Therefore, the gel effect is more important in the first moments of the reaction. The gel effect appears when the mobility of the growing chains is strongly reduced by the high medium viscosity, which drastically reduces the rate of chain termination, leading to the autoacceleration of the polymerization. The abrupt rise of the reactor temperature is caused by the gel effect, as shown in Figure 1. On the other hand, the glass effect seems to be more significant at the end of the reaction, when high monomer conversions are attained. In this case, the freezing of the reaction system and the existence of a maximum conversion limit arise as a consequence of the glass effect, characterized by the decrease of the propagation rates due to a decrease of the mobility of the monomer molecules in a highly viscous reaction medium, which normally leads to reduction of the overall reaction rates.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Behavior of the VAc/AA Copolymerizations.}
\end{figure}
Figure 2 illustrates the evolution of spectra collected during the batch copolymerization carried out in suspension process, containing 20% AA feed composition. It is clearly observed that appreciable changes in spectra take place along the batch. It is very important to notice that spectral changes associated with the process variables of interest are very useful for determination of calibration curves, which relate the spectral evolution during the batch and the desired polymer properties, allowing for the monitoring of polymerization reactions.

Figure 2 – Typical Spectral Changes During VAc/AA Copolymerizations.

Figure 3 shows the spectra of main reactive species inside the reactor during the copolymerization. As can be seen, the spectra are very different in the whole range of wavelength recorded. These differences in the individual spectrum of the reaction constituents are very beneficial to the spectral treatment. As a consequence, good calibration models can be obtained.

Figure 3 – Spectral Data from Reaction Medium Species. (A) Absorbance; (B) Second Derivative of Absorbance.
Several spectra collected during VAc/AA batch copolymerization performed with AA initial feed content ranged from 2.5 to 20 wt % were used for interpretation of the suspension process. Due to the significant spectral variation during the batch reaction, the wavelength region between 1500 and 1750 nm was considered important for spectral treatment. Figure 4 presents the spectra obtained during the copolymerization reaction containing 10% AA feed composition. As one can observe, the spectra of the reaction medium change during the whole batch, indicating the continuous decrease of the concentration of the reactive species and the gradual formation of the copolymer material. The spectral evolution with the copolymerization time is evidenced in Figure 4B.

The experimental collected data were divided into two main groups. The first one was used to build the calibration models, while the second group was employed in the validation step. Multivariate calibration techniques for NIRS analyses assume a linear relation between the parameters and the intensity of the absorption band related to the first and/or second derivative of the absorbance.\[22\] Mathematical techniques as partial least squares (PLS) present as main advantages: models can be utilized when process responses are functions of multiple process disturbances, correlating more than one predicted variable and different state variables;\[23-26\] calibration models can be built based on the whole defined spectral region, being generally used when the user does not determine wavelengths set that should be used to build the multivariate model.\[7\] In addition, both first and second derivatives of absorbance are useful for correction of baseline and favor the peaks resolution. In this work, the second derivative of absorbance was used in order to build the calibration curves (see Figures 5 and 6).
Spectra recorded during VAc/AA batch copolymerizations were used to build calibration models. The copolymerization reactions were carried out with AA initial feed content ranging from 2.5 to 20 wt %. Experimental data regarding the monomer concentrations inside the reactor were correlated to spectral evolution of the absorbance of the reaction medium and used to build regression curves based on the PLS technique.

![Graph A](image1)

![Graph B](image2)

![Graph C](image3)

**Figure 5** – Performance of PLS Calibration Models for Reactor Species. (A) Acrylic Acid; (B) Vinyl Acetate; (C) Polymer.

The spectral data of the reaction medium were mathematically treated using the NSAS software.\textsuperscript[21] According to Figure 5, the concentration of the reaction constituents can be successfully monitored, as very good PLS calibration models could be obtained for the AA aqueous concentration, the VAc in the organic phase and the polymer composition, based on available NIR spectra. Figure 6 illustrates the capacity of the calibration models to predict the concentrations of the chemical species for samples not used for calibration. The validation of the calibration models was performed using experimental data and NIR spectra of the second group. As can be seen, the calibration model obtained with the first group of experimental data is able to describe very well the
concentration of reactive constituents inside the reactor. This indicates that NIRS technique can be successfully used for monitoring and control of VAc/AA suspension process.

![Graphs showing calibration and validation results for Acrylic Acid, Vinyl Acetate, and Polymer](image)

**Figure 6** – Validation of PLS Models for Reactor Species. (A) Acrylic Acid; (B) Vinyl Acetate; (C) Polymer.

**Conclusions**

It was showed that NIRS technique can be successfully used to monitor VAc/AA suspension copolymerizations and that very good calibration model could be developed, describing very well the concentration of reactive constituents inside the reactor. The obtained calibration and validation results indicate that NIRS can be employed for suspension processes intended for process monitoring and control of copolymer composition in VAc/AA copolymerizations performed in suspension reactors.

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