

EMULSION COPOLYMERIZATION OF ACRYLONITRILE AND BUTADIENE IN AN INDUSTRIAL REACTOR. MATHEMATICAL MODELING, ESTIMATION, AND CONTROL OF POLYMER QUALITY VARIABLES ON THE BASIS OF CALORIMETRIC MEASUREMENTS

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Abstract— An industrial emulsion copolymerization of acrylonitrile and butadiene carried out in a batch (or semibatch) reactor for the production of nitrile rubber (NBR) is investigated. The effect of variable amounts of deactivating impurities on the predictions of a global polymerization model is analyzed; and the advantages of using the model predictions in combination with on-line calorimetric measurements are shown. The adjusted polymerization model allows to adequately monitor main quality variables of the process, such as: monomer conversion, average copolymer composition, average molecular weights, and degree of branching. The semibatch addition of the comonomers and/or the chain transfer agent along the reaction was investigated with the aim of controlling the polymer quality characteristics and increasing the productivity. It is possible to obtain a uniform-composition copolymer with pre-specified profiles of the average molecular weights or the degrees of branching. Furthermore, the NBR productivity can be increased by about 5%, without deteriorating the final copolymer quality with respect to that produced in the more conventional batch operation.

Keywords— Emulsion Copolymerization, NBR, Mathematical Model, Calorimetric Estimations, Polymer Quality Control.

I. INTRODUCTION

The emulsion copolymerization of acrylonitrile (A) and butadiene (B) for the production of NBR is investigated with the aim of estimating the evolution of the main reaction variables and of improving the rubber quality. Such quality is determined by the average values of the copolymer composition, the molecular weights, and the degrees of branching.

Several NBR grades are produced via the “cold” emulsion polymerization process, that mainly differ in their copolymer composition and average molecular weights (Kirk and Othmer, 1981). Batch reactors are generally employed, but semibatch reactors and trains of continuous stirred-tank reactors are also used. Even

though NBR has been produced through the emulsion process for more than 50 years, many scientific aspects of its synthesis and characterization still remain unknown.

In general, the polymer quality is improved when the copolymer composition is kept constant along the reaction, and when the levels of branching and cross-linking are maintained below certain values. The degrees of branching and gel contents are normally limited by keeping the monomer conversion below 80%. The most common NBR grade (BJLT), contains a global mass fraction of A of approximately 35%. This value is close to the azeotropic composition (38%), and therefore a small compositional drift is produced under a batch operation. In contrast, other NBR grades with mass fractions of A between 15–34%, exhibit decreasing compositions along the reaction, while increasing composition profiles are observed for global compositions over 38%. The molecular weights are limited by including a chain transfer agent (CTA) or “modifier” in the reaction recipe (Ambler, 1973).

In the standard practice, NBR processes are monitored from on-line reaction temperature measurements in combination with off-line measurements of conversion, copolymer composition, and Mooney viscosity. The presence of varying amounts of impurities like oxygen in the reaction system determines that relatively large batch-to-batch variations are observed. Two global mathematical models for the emulsion copolymerization of A and B have been presented (Dubé *et al.*, 1996; Vega *et al.*, 1997). In Rodríguez *et al.* (2002) a detailed mathematical model is presented that allows to estimate the molecular weight distributions of each generated branched topology and of the NBR produced along the reaction. Such models are incapable of predicting the real evolution of the NBR process variables in the presence of unknown amounts of reactive impurities. The model predictions can be considerably improved if the conversion is on-line measured or estimated, by using for example gas chromatography, densitometry, Raman spectroscopy or reaction calorimetry.

For the emulsion copolymerization of A and B, the estimation of polymer quality variables (monomer con-