EMULSION COPOLYMERIZATION OF ACRYLONITRILE AND BUTADIENE IN A TRAIN OF CSTRS. INTERMEDIATE ADDITION POLICIES FOR IMPROVING THE PRODUCT QUALITY

R.J. MINARI, L.M. GUGLIOTTA, J.R. VEGA, and G.R. MEIRA

INTEC (Universidad Nacional del Litoral – CONICET), Güemes 3450, (3000) Santa Fe, Argentina
lgug@intec.unl.edu.ar

Abstract- **A continuous industrial emulsion copolymerization of acrylonitrile (A) and butadiene (B) carried out in a train of 8 continuous stirred-tank reactors (CSTRs) at 10 °C is theoretically investigated, with the aim of producing nitrile rubber (NBR) of a quality similar to that obtained in an equivalent batch process. The rubber quality is specified by the latex characteristics (number particle concentration and number-average particle diameter), and by the molecular parameters (average values of the copolymer composition, the molecular weights, and the degree of branching). A mathematical model of the NBR industrial batch process is here extended for simulating the operation of the CSTR train. Two NBR grades of a different chemical composition are investigated. Compared with the batch product, the continuous Normal Steady State (SS) operation, with the complete recipe fed into the first reactor of the train, produces a deteriorated rubber (higher polydispersity and higher degree of branching). Such undesirable effects can be corrected through intermediate additions of A and chain transfer agent (CTA) along the continuous train. Finally, the reduction of the off-spec product generated during the change of grade between Normal SSs is also investigated. To this effect, "bang-bang" strategies for the comonomers and the CTA feeds in the first reactor of the train allow reducing up to 30 % of the off-spec product generated when a simple step change in all the feeds is applied.**

Keywords: **Emulsion Copolymerization, Reactor Train, Composition Control, Molecular Weight Control**

I. INTRODUCTION

Nitrile rubber or NBR is industrially produced by polymerizing A and B through the "cold" emulsion process (Kirk and Othmer, 1981). The reaction system can be either a batch (or semibatch) reactor, or a train of CSTRs, when high production levels are required.

The molecular characteristics of NBR are mainly determined by the copolymer composition, the molecular weights, and the degree of branching. The most common NBR grade (BJLT) contains a total mass fraction of bound A ($\bar{p}_A$) of about 35%. This value is slightly lower than the azeotropic composition of 38% (Ambler, 1973), and therefore a moderate compositional drift along the reaction is normally observed. The CJLT grade is closer to the azeotrope, and for this reason $\bar{p}_A$ is practically uniform. The AJLT grade has a $\bar{p}_A$ value of about 20%, and it exhibits an important compositional drift that produces a deteriorated rubber with multiple glass transitions (Guyot *et al.*, 1984). Many composition control strategies have been developed. For instance, Vega *et al.* (1997) controlled the compositional drift of a BJLT grade through a semibatch policy that considered impulsive additions of A along the reaction.

The molecular weights are usually limited by adding a chain transfer agent (CTA) in the reaction recipe (Ambler, 1973). Also, the degree of branching is maintained under 1 branch per molecule by limiting the final conversion to around 75%. While the number-average molecular weight ($\bar{M}_n$) remains practically constant, both the weight-average molecular weight ($\bar{M}_w$) and the average number of trifunctional branches per molecule ($\bar{B}_{n3}$) increase along the reaction, producing a higher final polydispersity.

Mathematical models of the NBR emulsion process for predicting the average molecular properties ($\bar{p}_A$, $\bar{M}_n$, $\bar{M}_w$, $\bar{B}_{n3}$) have been reported by Dubé *et al.* (1996), Vega *et al.* (1997), and Rodríguez *et al.* (2002). The model by Vega *et al.* (1997), has been recently applied for estimating conversion and average molecular properties, on the basis of calorimetric measurements taken in a semibatch industrial process (Gugliotta *et al.*, 1999; Vega *et al.* 2002). In Vega *et al.* (2002) control strategies were developed for producing NBR with predetermined profiles of copolymer composition and average molecular weights.

Several articles have investigated the optimization and control of a CSTR train for the production of styrene-butadiene rubber (SBR), but the problem of the continuous production of NBR has not yet been addressed. For the SBR process, Vega *et al.* (1995a) and Minari *et al.* (2006) improved the polymer production by splitting the comonomers mixture feed into the first reactors of the train. Also, they control the final quality properties by intermediate SS additions of CTA. While Vega *et al.* (1995a) imposed a constant