

Continuous emulsion copolymerization of acrylonitrile and butadiene Computer simulation study for improving the rubber quality and increasing production

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Abstract

This theoretical article investigates an industrial emulsion copolymerization of acrylonitrile (A) and butadiene (B), for the production of grades BJLT and AJLT of a nitrile rubber (NBR). The simulated process involves a train of eight continuous stirred-tank reactors operating at 10 °C. The product quality is determined by its molecular structure (average copolymer composition, average molecular weights, and average level of branching), and by its final latex characteristics (number particle concentration and number-average particle diameter). The mathematical model by Vega et al. [Vega, J. R., Gugliotta, L. M., Bielsa, R. O., Brandolini, M. C., & Meira, G. R. (1997). Emulsion copolymerization of acrylonitrile and butadiene, mathematical model of an industrial reactor. *Industrial and Engineering Chemistry Research*, 36, 1328] for the semibatch process was extended to investigate three alternative steady-state (SS) operations of a continuous reactor train. When all the reagents are fed into the first reactor (Normal SS), then a deteriorated quality compared with respect to the equivalent batch process is produced (with increased polydispersities and degrees of branching). This can be improved by admitting intermediate feeds of A and chain transfer agent (CTA) along the train. If in addition, constant B feeds are admitted, then it is possible to eliminate the compositional drift, to generate predetermined profiles of the average molecular weights, and to increase the rubber production by over 10% with respect to the Normal SS. The best improvements were observed for grade AJLT. © 2006 Elsevier Ltd. All rights reserved.

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1. Introduction

Nitrile rubber (NBR) is industrially produced by copolymerizing acrylonitrile (A) and butadiene (B) in the “cold” emulsion process. Such process can be carried out in batch, semibatch, or continuous reaction systems (Kirk & Othmer, 1998). Table 1 presents the main characteristics of some typical NBR grades; with all the names containing the letter “J” to indicate that they exhibit a common Mooney viscosity. For increased mass fractions of A in the copolymer, the following also increase: (a) the glass transition temperature (T_g) (Table 1) and (b) the resistances to fuels and solvents, to abrasion, and to gas permeation. The Mooney viscosity depends on the molecular weights, on the degrees of branching, on the copolymer composition, and on the

presence of low molecular weight additives such as mineral oil (Kensuke, Tsutomu, Mitsuru, Tooru, Mitsutoshi, & Nobuyuk, 1977; Nobuo, 1984).

In the NBR emulsion process, the molecular weights are controlled by addition of a chain transfer agent (CTA); and the monomer conversion (x) is limited to around 80% to maintain the average degree of branching below 1 branch per molecule (Kirk & Othmer, 1998). The monomer conversion greatly affects the molecular properties of the produced rubber (average molecular weights, degrees of branching, and chemical composition). Compositional drifts are undesirable because they can induce phase separations and multiple glass transitions (Guyot, Guillet, Craillat, & Llauro, 1984). At 38% of A with respect to the total comonomer mass (the azeotropic composition), the copolymer composition remains constant along a batch copolymerization (Ambler, 1973). For grade CJLT, the lower limit of it's a content specification coincides with the azeotropic composition (Table 1); and for this reason this grade can be easily produced

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Table 1
Properties of four typical NBR grades

Grade	AJLT	BJLT	CJLT	DJLT
Mass fraction of A (%)	18–22	30–35	38–42	43–46
Mooney viscosity (MS) ^a	40–52	40–52	40–52	40–52
T_g (°C)	–56	–37	–27	–22

^a Mooney Scorch.

in batch reactors. In contrast, large compositional drifts are expected in the batch production of grade AJLT, with a decreasing mass fraction of A in the copolymer.

The NBR emulsion process has been previously modeled by Dubé, Penlidis, Mutha, and Cluett (1996), Vega et al. (1997), and Rodríguez, Estenoz, Gugliotta, and Meira (2002). Vega et al. (1997) investigated the industrial batch production of grade BJLT with *tert*-dodecyl mercaptan as CTA. They observed that while the number-average molecular weight (\bar{M}_n) remained essentially constant along the reaction, the weight-average molecular weight (\bar{M}_w) and the average number of trifunctional branches per molecule (\bar{B}_{n3}) both steadily increased. Also, an almost constant chemical composition could be produced by applying several discrete pulses of A (*i.e.* varying amounts of A added along short periods of time). The model by Vega et al. (1997) was later applied in Gugliotta, Vega, Antonione, and Meira (1999) and in Vega, Gugliotta, and Meira (2002), for estimating the monomer conversion, the copolymer composition, the average molecular weights, and the average degree of branching, on the basis of calorimetric measurements. In Vega et al. (2002), several (model-based and closed-loop) semibatch strategies were developed for controlling such estimates.

Styrene–butadiene rubber (SBR) is normally produced in continuous emulsion processes; and several articles have been published in relation with their steady-states (SSs) and dynamic control. In contrast, no publications have been found on the continuous production of NBR. For continuous emulsion processes, Hamielec and MacGregor (1983) proposed to feed the comonomers mixture into the first reactors of the train for maximizing the polymer production by reducing the total “inert” monomer droplets volume. Following this idea, Vega, Gugliotta, Brandolini, and Meira (1995) and Minari, Vega, Gugliotta, and Meira (2006) suggested to simultaneously feeding CTA along the train for improving the final SBR quality.

This theoretical work optimizes the SS operation of a continuous NBR process with the aims of: (i) eliminating the copolymer compositional drift and reproducing the average molecular weights of an equivalent batch process, without imposing a fixed final monomer conversion and (ii) increasing the polymer production, at a fixed final conversion, while simultaneously eliminating the compositional drift and reproducing the final molecular weights, degrees of branching, and particle characteristics of an equivalent batch process.

2. Batch processes and Normal SS operations

Two plants, property of Petrobras Energía S.A. (Pto. Gral. San Martín, Argentina) were investigated: a batch reactor for producing NBR, and a train of up to 13 continuous stirred-tank reactors

(CSTRs) that is normally employed for producing SBR. The batch reactor volume was 17,473 L, while each of the CSTRs in the train exhibited a reaction volume of 17,473 L. In both cases, the reaction temperature was controlled at 10 °C. This work deals with optimizing the continuous plant for producing NBR.

2.1. Grade BJLT

Following Vega et al. (2002), the batch recipe and final latex properties of grade BJLT are given in the second column of Table 2. In Table 2, \bar{p}_A/\bar{p}_{An} represents the compositional polydispersity, where \bar{p}_A and \bar{p}_{An} are the weight- and number-average mass fractions of A in the copolymer, respectively. Also, A_E/A_p is a measure of the latex stability, since it represents the fraction of particles area recovered by the emulsifier.

The batch model by Vega et al. (1997) was here extended to simulate the continuous production of NBR in a train of eight CSTRs. The model parameters were identical to those of Vega et al. (2002), and for this reason they are not reproduced here. We define a “Normal” SS operation as that where all the reagents are fed into the first reactor only. The recipe and simulation results of the Normal SS operation are in the third column of Table 2. Except for the initiator concentration, all the other reagent concentrations coincide with the batch reaction values. The initiator concentration and total volume feed rate q_T , were adjusted to reproduce the final batch values of the global conversion x , the particle diameter \bar{d}_p , and the ratio A_E/A_p . In the Normal SS, note that the final values of x , \bar{d}_p , and A_E/A_p coincide with the required batch values, and that the final compositional polydispersity (represented by the ratio \bar{p}_A/\bar{p}_{An}) also coincides with that of the batch (Table 2). The molecular characteristics are in general similar to that of the batch, except for somewhat larger values of \bar{M}_w/\bar{M}_n and \bar{B}_{n3} ; due to the wider distribution of residence times of the continuous process. In the continuous process, the polymer chains that remain longer than the overall residence time, increase their probability of branching in an exponential fashion, thus increasing \bar{B}_{n3} and \bar{M}_w . In Table 2, V_d (=13,200 L) represents the total monomer droplets volume (that according to our polymerization model it is distributed among the first four reactors of the train).

2.2. Grade AJLT

Consider now the batch and Normal SS operations of grade AJLT. The recipes are in the second and third columns of Table 3. In the Normal SS, the total volume feed rate q_T and the initiator concentration were adjusted for reproducing the final batch values of x , \bar{d}_p , and A_E/A_p . As before, the final molecular characteristics are in general deteriorated with respect to the batch, with increased values of \bar{M}_w , \bar{M}_w/\bar{M}_n , and \bar{B}_{n3} . Also as expected from the reactivity ratio values, the final compositional polydispersities are considerably larger than in grade BJLT (Table 3).

3. Improved steady-states

Consider improving the Normal SS operations, by admitting intermediate constant feeds of A, B, and CTA. The proposed

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