Control of Microstructural Properties in Emulsion Polymerization Systems

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Summary: Control strategies for the simultaneous control of microstructural properties of copolymer latexes (copolymer composition and molecular weight distribution) are presented. For linear polymers, on-line control strategies based on calorimetric measurements allowed to produce styrene/n-butyl acrylate emulsion polymers of predefined copolymer compositions and MWDs. The strategy failed for nonlinear polymers because the polymer produced at a certain process time might later in the process become active varying its molecular weight. Alternative open-loop control policies were developed for nonlinear polymers. These strategies required a mathematical model of the process that is used in an off-line optimization to determine the trajectories of the manipulated variables (feed flow rates of monomer and CTA) that allow producing the desired copolymers. The implementation of the open-loop control allowed the production of nonlinear MMA/n-BA emulsion copolymers of well-defined copolymer composition and MWD.

Introduction

End-use properties of polymer latexes are intimately related to the microstructure of the polymer, namely polymer composition, molecular weight distribution, branching frequency (short and long branches), crosslinking and gel content in addition to other properties such as particle morphology and particle size distribution. These microstructural properties must be maintained in well-defined values to produce polymers useful for the demanding commercial applications. This usually requires controlling several of these properties throughout the course of the polymerization, namely, in the polymerization reactor. However, on-line and/or closed-loop control of more than one microstructural property is not common in industrial practice and scarcely reported in the open literature, where this is

 CCC 1022-1360/00/$ 17.50+.50/0

mainly done on simulation basis.

Every year dozens of new products and applications that meet the market needs are produced by industry. These polymers, that have a combination of microstructural properties that make them so useful and profitable, are often produced by open-loop control strategies that are prone to batch-to batch irreproducibility, and hence the consistency of the polymer quality is not guaranteed. In addition, this way of conducting the process involves the risk of thermal runaways.

There is a strong need for substituting this practice by on-line and closed-loop control strategies that offer the possibility of achieving the required polymer properties in the polymerization reactor, thus reducing the number of off-spec batches and allowing to produce polymers with a tighter control of the microstructural properties in a safer fashion.

This paper is a summary of the recent efforts made in our group towards the development of on-line and closed-loop control strategies for controlling microstructural properties of copolymer latexes of industrial significance. Control strategies to produce latexes of well defined composition and molecular weight distribution in linear and nonlinear (branched) polymer systems are presented. Unsolved issues and future challenges are also discussed.

Linear Polymers

Copolymer composition is by far the microstructural property that has been more often controlled. To achieve this goal the ratio of the comonomers in the polymerization loci should be controlled. Open-loop strategies, based on mathematical models or on extensive experimental work[1-4] and closed-loop strategies using different on-line sensors[5-11] have been presented in the last two decades to control copolymer composition. Closed-loop control strategies based on calorimetric measurements[9-11] are specially suited for implementation in an industrial environment.

The control of the MWD of emulsion polymers by means of closed-loop strategies is a challenging subject because the feasibility of the on-line measurement of the MWD for emulsion polymerization systems remains to be demonstrated. In addition, the compartmentalized nature of the emulsion polymerization makes, generally speaking, the

MWD non-observable from usually available on-line measurements (monomer conversion, temperatures and polymerization rate). Nevertheless, under some conditions of practical significance, the MWD of emulsion polymers is not affected by the compartmentalization of the system. A typical example is when a chain transfer agent is used and the kinetic chain length is controlled by chain transfer to chain transfer agent (CTA). Storti and Morbidelli[12] used this circumstance to keep constant the MWD of the polystyrene latex during the whole polymerization. A characteristic feature of linear polymers is that once they are formed in polymerization they do not suffer any reaction that modifies their structure. This feature can be advantageously used to produce latexes of any MWD by sequentially forming polymer of different instantaneous MWDs. Thus, Echevarria et al.[13] produced polystyrene latexes of well defined MWD by varying the monomer/CTA ratio in such way that long chains were produced at the beginning of the process whereas the short ones were obtained in the last stages of the polymerization. A drawback of the technique used by these authors[13] is that the on-line measurements of styrene and CTA were carried out using invasive techniques that are difficult to implement in an industrial environment.

Reaction calorimetry[14-18] is an appropriate technique for on-line monitoring of polymerizations, since these reactions are very exothermic. The measurement is non-invasive, rapid and robust as it is based on temperature measurements. Although reaction calorimetry does not provide a direct measurement of the unreacted amount of monomer in the reactor, state observers and estimators allow the estimation of the unreacted amounts of monomers and chain transfer agent. Gugliotta et al.[19] and Sáenz de Buruaga et al.[9-11] using open-loop observers showed that the estimation of the unreacted amounts of monomers in batch and semicontinuous emulsion copolymerizations is accurate enough as to be used in strategies to control the composition of co/terpolymers. Vicente et al.[20] extended the use of open-loop observers based on calorimetric measurements to estimate the unreacted amount of chain transfer agent in the reactor and applied the control strategy developed by Echevarria et al.[13] to successfully on-line control the MWD of polystyrene latexes.

All of the previously discussed control strategies were developed to control a single microstructural property. Only few works have been published on the simultaneous control of MWD and copolymer composition in free radical copolymerization and even less were

experimentally tested. The work of Vicente et al.[21] is the only one where the copolymer composition and the entire MWD are on-line controlled for an emulsion copolymerization system.

The control strategy employed is summarized in Figure 1. The heat of polymerization calculated on-line from a modified RC1 reactor calorimeter (Mettler-Toledo) is used to infer the concentrations of unreacted monomers and CTA in the reactor, by means of an open-loop observer based on material balances. The estimated states are compared with optimal trajectories calculated off-line using the desired copolymer composition and MWD as constraints. This information is then used by a nonlinear model based controller to calculate the flow rates of monomers and CTA that allow the process to track the optimal trajectories.

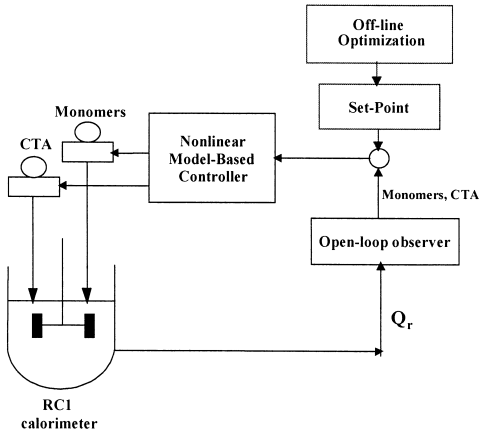
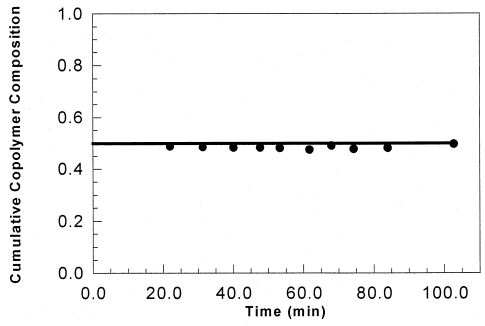


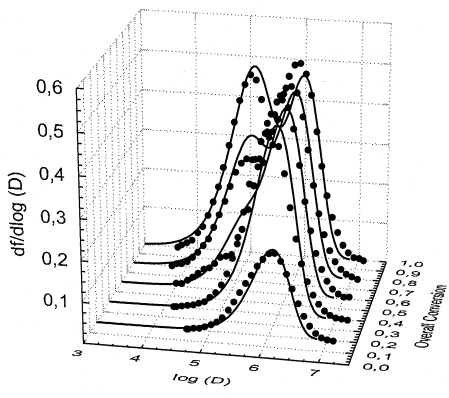
Fig. 1 Schematic of the control strategy used to simultaneously control polymer composition and MWD of linear polymers. (Ref. 20 and 21).

This control strategy was validated in real-time experiments by producing styrene/n-butyl acrylate copolymers of different compositions and molecular weights. An example is presented in Figure 2. The copolymer sought was a styrene/n-butyl acrylate copolymer of composition 50/50 and a bimodal MWD (mode 1; $\overline{M}_{w1}$ =1,050,000 and PI=2,5 and Mode 2; $\overline{M}_{w2}$ =115,000 and PI=3). Figure 2a presents the time evolution of the cumulative copolymer composition produced along the polymerization and Figure 2b compares the

target MWD and those produced at different stages of the polymerization. As shown in the figure the polymer produced had the desired quality. Similar results were obtained for other compositions and MWD shapes.



a)



b)

Fig. 2 a) Time evolution of the cumulative copolymer composition. Legend: (——) desired; (●) experimental. b) Evolution of the MWD produced at different conversion. Legend: (——) desired; (●) GPC traces. (Ref. 21).

The direct application of this control strategy to industrial reactors may be risky because the heat generation rate was not taken into account. In an industrial reactor, due to the small

heat exchange area/reactor volume ratio, the control of the temperature is generally difficult. Therefore, the process should be conducted in such a way that the desired copolymer composition and MWD are produced at a rate that does not jeopardize the thermal control of the reactor.

Let us consider an industrial reactor where the cooling capacity is regulated through the temperature of the cooling fluid entering the reactor jacket. This temperature can be varied by mixing cold water with steam. The nominal maximum cooling capacity of the reactor is achieved when no steam is introduced in the system. For this reactor, the optimal process should be conducted in such a way that the desired copolymer composition and MWD are obtained at the predefined reactor temperature (to maintain all the product properties achieved during the development of the formulation) using the nominal maximum cooling power.

When the maximum heat removal rate is known, the implementation of an on-line strategy for such a process requires including an additional constraint that forces the process to track the trajectory of the maximum heat removal capacity of the reactor. This new control strategy was validated for the emulsion copolymerization of styrene and n-butyl acrylate. The maximum heat removal rate per unit of volume of a large scale reactor, Q_{rmax}, was scaled down and tracked in a lab reactor. A copolymer latex of styrene/n-butyl acrylate of the desired composition was produced (50/50 molar composition and MWD with polydispersity index, PI=2 and $\overline{M}_w = 4x10^5$ g/mol) using tert-dodecyl mercaptan as CTA.

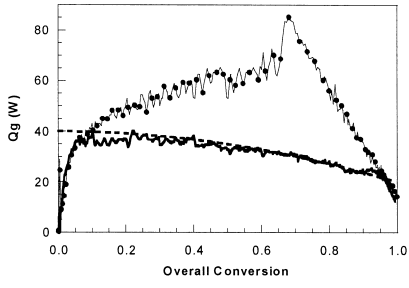


Fig. 3 Comparison of the evolution of the heat rate generated during the reaction (Q_g —) with the maximum heat removal capacity of the reactor (Qr_{max} - - -) and the heat generated in a similar experiment without controlling heat generation rate (—●—). (Ref. 22).

Figure 3 shows that the heat released by polymerization was maintained at the desired maximum trajectory throughout the whole process, something that was not achieved when the heat removal limit was not introduced in the control strategy[22].

When the maximum heat removal capacity of the industrial reactor is not accurately known or not enough information is available, the strategy presented above cannot be applied. In these cases, the approach presented by Asua[23] that used a hierarchical fuzzy logic/model-based controller for achieving maximum and consistent production of emulsion polymers under safe conditions is very suitable.

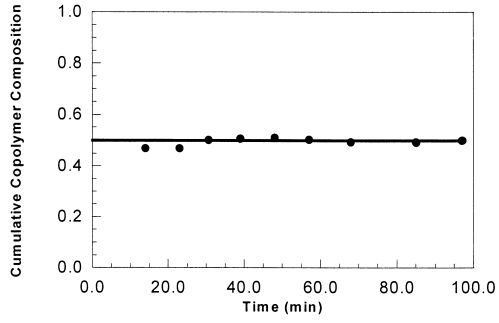
Nonlinear Polymers

Nonlinear (branched) polymers are those in which there are side branches or linked monomer molecules protruding from various central branch points along the main polymer chain[24]. The branched polymer can be comblike in structure with either long or short branches. When there is extensive branching, the polymer can have a dendritic structure in which there are branches protruding from other branches. If branched polymer chains can be linked to other similar branched polymer chains, the polymer formed is known as a crosslinked polymer. Branching in radical polymerization might occur if one of the following mechanisms is significant during the polymerization: i) chain transfer to polymer, ii) propagation to terminal double bonds, iii) β scission, and/or iv) divinylic monomers are used.

In these systems, inactive polymer chains can be reactivated by any of the above mentioned mechanisms modifying their structure (molecular weight), and hence the desired MWD cannot be decomposed in a series of instantaneous MWDs produced at different stages of the process.

Therefore, control strategies as those developed for linear systems will fail unless one works under conditions in which the branching mechanism is not significant during the polymerization. This was demonstrated recently by Vicente et al.[25] when they tried to implement the control strategy developed for linear polymers to produce a MMA/n-BA copolymer having a composition of 50/50 with a weight-average molecular weight of

400,000 g/mol and minimum polydispersity index (PI=2). Figure 4 shows the results obtained in the attempt. Although the copolymer composition was well controlled (Figure 4a), the weight-average molecular weight deviated from the target value from the very beginning of the process (Figure 4b). The reason is that branched polymers were formed by intermolecular chain transfer to polymer. Note that the number-average molecular weight was not affected by the process because the total number of chains is not affected by the chain transfer to polymer.



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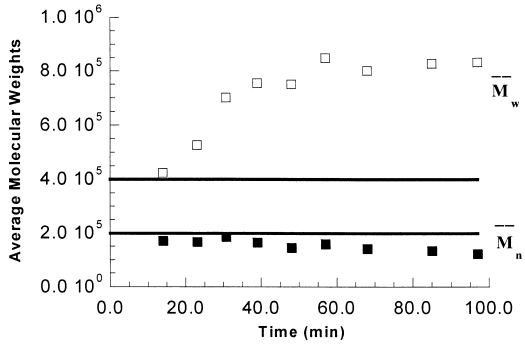


b)

Fig. 4 Time evolution of the cumulative copolymer composition (referred to MMA, Figure 4a) and cumulative average molecular weights(Figure 4b). Legend: desired values (——) and experimental results (●, ■, ❑). (Ref. 25).

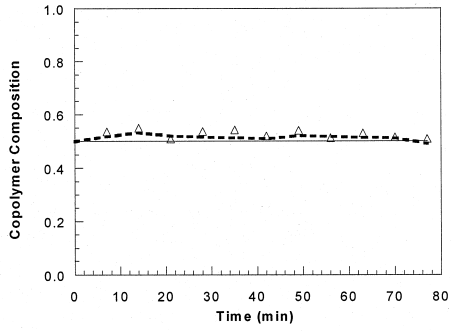
Better results using this control strategy can be obtained by carrying out the polymerization under semi-flooded conditions, because chain transfer to polymer is minimized when chain transfer to CTA becomes again the larger chain stopping termination event. However, these polymerization scenarios are prone to give thermal runaway, and hence are too risky to be implemented in industrial reactors.

An additional difficulty for the control of the entire MWD of nonlinear polymers is that the off-line measurement of the MWD of nonlinear emulsion polymers might take several hours (solvent extraction might be necessary if gel is present) precluding the use of multi-rate state observers[26] to estimate the molecular weight. Furthermore, the on-line estimation of the MWD of nonlinear polymers is an unsolved issue, and hence the implementation of real-time close-loop strategies for controlling the MWD of nonlinear polymers cannot be currently envisaged.

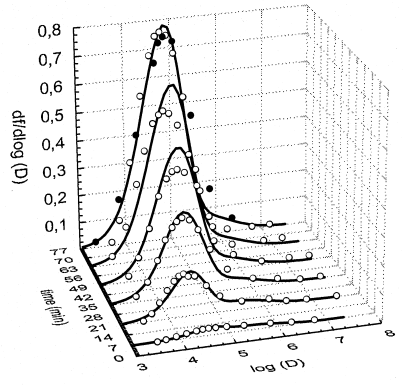
Under these circumstances, open-loop control offers a pragmatic alternative. The time varying control variables to be implemented in the open-loop strategy can be calculated through process optimization using a mathematical model for the emulsion polymerization system. It is worth pointing out that the success of the open-loop strategy relies on both the accuracy of the mathematical model and the absence (minimization) of unmodeled process disturbances.

An extensive research program aiming at developing fundamental understanding of the mechanisms involved in the formation of the microstructure of nonlinear polymers is being carried out.[27-29] , and predictive mathematical models have been developed[30-33] These models were used to calculate the optimal strategies to produce MMA/n-BA emulsion copolymers of given MWDs. The optimization was performed by using an iterative dynamic programming, IDP, algorithm[34]. This algorithm presents the advantage of being able to handle constrained optimization of systems described by complex mathematical models, as those needed for nonlinear emulsion copolymerization systems. Vicente et al [35] have implemented these optimal strategies in open-loop control mode to produce MMA/n-BA copolymer of 50/50 molar constant composition and unimodal and bimodal distributions of very different polydispersities. Figure 5 shows the results obtained for the unimodal MWD ($\overline{M}_w = 3.5x10^5$ and $PI = 14$). Both the time evolution of the cumulative

copolymer composition (Figure 5a) and the evolution of the MWD at different stages of the process (Figure 5b) show that the required copolymer was produced.



a)



b)

Fig. 5 a) Time evolution of cumulative copolymer composition referred to MMA. Legend: (——) desired composition; (- - -) Composition calculated in the optimization; (Δ) experimental composition. b) Comparison between the evolution of the desired final MWD (●), the MWD obtained in the optimization (——) and the MWD obtained experimentally at conversions 5%, 18%, 36%, 57%, 78% and 96%.(○). (Ref. 35).

Future Challenges

The use of open-loop control strategies for nonlinear polymers is not a definitive solution because when the system is subjected to non-modeled disturbances, this type of strategy fails. Therefore, robust closed-loop control strategies should be developed. This requires developments in two areas. First, it is necessary to develop methods for on-line estimation of the MWD of nonlinear polymers. This would probably require the use of soft sensors based on a more accurate measurement of the concentrations of monomer and CTA in the reactor. In this regard, the combination of reaction calorimetry and Raman (or NIR) spectroscopy is promising. Second, the determination of the optimal trajectory to be tracked requires performing on-line optimization. The available optimization algorithms are not able to handle complex models in a manner rapid enough. Therefore, considerable effort should be devoted to develop more efficient optimization algorithms and to simplify the mathematical models currently available. In this regard, hybrid mathematical models (e.g., neural networks and material balances) are promising.

Acknowledgments

The financial supports from CICYT (project PPQ2000-1185) and the University of the Basque Country are gratefully appreciated. M. Vicente acknowledges the fellowship from the Spanish Government.

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