Batch Process Monitoring and Its Application to Polymerization Systems

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Summary: Slight changes in raw material properties or operating conditions during critical periods of operation of batch and semi-batch polymerization reactors may have a strong influence on reaction mechanism and impact final product quality. Online process monitoring, fault detection, fault diagnosis, and product quality prediction in real-time ensure safe reactor operation and warn operators about excursions from normal operation that may lead to deterioration in product properties. Multivariate statistical process monitoring and quality prediction using multiway principal components analysis and multiway partial least squares have been successful in detecting abnormalities in process operation and product quality. When abnormal process operation is detected, fault diagnosis tools are used to determine the source cause of the deviation. Illustrative case studies are presented via simulated polyvinyl acetate polymerization.

Keywords: statistical process monitoring; quality prediction; radical polymerization; modeling; batch processes

Introduction

Many polymers are produced by using batch and/or semi-batch reactors through a number of operational phases. A high degree of reproducibility in product quality is necessary to obtain successful batches. Slight changes in operating conditions during critical periods of a batch run may have a significant influence on reaction mechanism, and impact final product quality. Changes in feed properties and impurity levels also affect the final product. The temporal variability in batch polymerization reactors may cause the broadening of molecular weight distribution and in the case of copolymers,

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compositional drifts. Online process performance monitoring and product quality prediction in real-time can reduce quality variations. Early detection of excursions from normal operation that may lead to deteriorated products, diagnosis of the source cause(s) of the deviation, and prediction of product quality in real-time ensure safe and profitable operation, and provide the opportunity to take corrective action before the effects of disturbances ruin the batch. Process variable trajectories contain valuable information for monitoring the performance of the process and can also be related to product quality measurements that usually become available at the end of a batch run. Multivariate statistical projection methods such as principal component analysis (PCA) and partial least squares (PLS) have been useful in developing multivariate statistical process monitoring (MSPM) and quality prediction techniques.[1,2] These techniques have become a powerful alternative to conventional univariate statistical process control (SPC) and statistical quality control.

Analysis of batch process data offers a variety of challenges. It is common that the total duration of various batch runs and/or the duration of individual phases within a batch run are not the same, caused by seasonal changes in environmental variables (e.g. coolant temperature variations), variations in quality and impurity concentrations of raw materials, and arbitrary termination of batches by plant operators. The unequal batch data length causes problems for vector-matrix calculations involved in empirical modeling. In addition, critical local features (process landmarks) in process variables in each batch run corresponding to certain phases of process dynamics may occur at different times resulting in unsynchronized batch profiles. These shifts can affect monitoring activities and generate false alarms. Alignment of landmarks is necessary for comparing similar events. *Dynamic time warping* (DTW)[3], *curve registration*[4] and *indicator variables*[5,6] methods have been suggested to synchronize and align batch trajectories. Comparison of these techniques in MSPM has been reported.[7]

Batch process measurements made on J variables at K time intervals for I batches

that resulted with acceptable product quality form a three-way array $\underline{\mathbf{X}}$ of size $(I \times J \times K)$. Product quality measured at the end of batch with M variables form a matrix $\mathbf{Y}$ of size $(I \times M)$. PCA and PLS techniques have been extended to multiway PCA (MPCA) and multiway PLS (MPLS) to account for this three-way data array decomposition of batch processes.[8] MSPM techniques based on trilinear decompositions of $\underline{\mathbf{X}}$ such as parallel factor analysis (PARAFAC), and Tucker models have also been suggested.[9–11] Applications in batch/semibatch polymerization have been reported.[12,13]

Online batch process monitoring is challenging because early techniques used future portions of process variable trajectories that are not available during the progress of the batch. Different approaches have been used to fill future parts of these trajectories based on some assumptions including the use of missing value prediction capabilities of PCA and PLS. Each assumption introduces some level of arbitrariness and should be chosen based on the process and disturbance type. These approaches have been incorporated into MPCA and MPLS.[12–15] Techniques that do not require future value estimation have been proposed.[11,16–18] One of these techniques establishes a different online MSPM framework based on unfolding the three-way data array by preserving variable direction.[17,19–21] In this approach, MPCA or MPLS models can be developed for online monitoring by unfolding the three-dimensional process variables matrix $\underline{\mathbf{X}}$ to a two-dimensional matrix $\mathbf{X}_{\mathbf{v}}(IK \times J)$.

A two-step MSPM framework is described in this study. First, $\underline{\mathbf{X}}$ (Fig. 1a) is unfolded by preserving variable direction ($\mathbf{X}_{\mathbf{v}}$, Fig. 1b) and modeled using MPCA for online SPM without requiring future value estimation. Then, $\underline{\mathbf{X}}$ is unfolded by preserving batch direction ($\mathbf{X}_{\mathbf{b}}$, Fig. 1c) to develop local MPLS models to predict end-of-batch quality (Fig. 1d) during the progress of the batch. DTW-based trajectory alignment is also integrated into the first step of the online MSPM technique.

The paper outlines the integrated MSPM framework. This includes description of DTW methodology and its integration with MPCA, followed by product quality

estimations using MPLS and contribution plots for identifying variables affecting the monitoring statistics to initiate fault diagnosis. Finally, the MSPM methodology is illustrated with a simulated polyvinyl acetate batch process.

Development of Integrated MSPM Framework

An appropriate reference data set is chosen which defines normal operation (NO) for a particular process based on the data collected from various batch runs when the performance is good. The integrated MSPM framework for both end-of-batch and online implementation consists of:

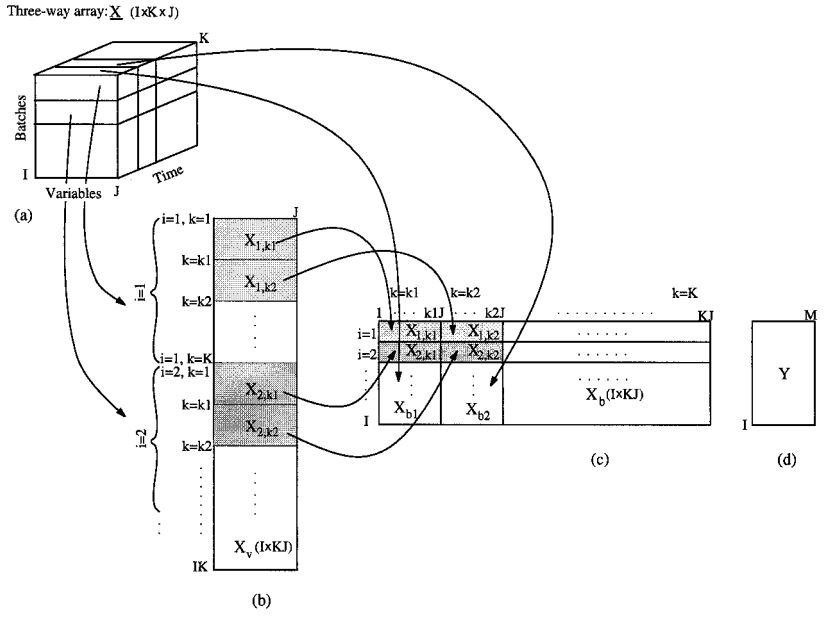

Figure 1. Data unfoldings for two-step MSPM, (a) Three-way array $\underline{\mathbf{X}}$, (b) unfolded array to $\mathbf{X_v}$ $(IK \times J)$ by preserving variable direction, (c) unfolded array to $\mathbf{X_b}$ $(I \times KJ)$ by preserving batch direction, (d) matrix $\mathbf{Y}$ of final quality measurements.

1. Alignment (synchronization) and equalization of batch trajectories
2. MPCA model development with reference batch data set ($\underline{\mathbf{X}}$ unfolded by preserving variable direction into $\mathbf{X_v}$ of size $IK \times J$)
3. Local MPLS model generation between aligned incremental data partitions matrix $\mathbf{X_{bi}}$ of size $I \times kiJ$ and final quality matrix $\mathbf{Y}$ of reference set
4. Construction of MV limits for both postmortem and online implementation
5. Online SPM and quality prediction of a new batch

Alignment and equalization of batch trajectories using Dynamic Time Warping (DTW). DTW is a deterministic pattern matching scheme which works with pairs of patterns. It has its origins in speech recognition. It is able to locally translate, compress, and expand the patterns so that similar features in the patterns are matched.[3,22,23] It nonlinearly warps two trajectories in such a way that similar events are aligned and a minimum distance between them is obtained. The objective of DTW is to find the nonlinear mapping function between two multivariate observation sets, (reference set and test set) subject to a set of path and end-point constraints to minimize the accumulated distance between them. Mahalanobis distance[3,22] can be used as a measure of local similarity between the points in test and reference sets. The distance includes $\mathbf{W}_p$ that reflects the relative importance of the p variables preferably based on their resemblance to time axis. Information about the reference batch, scaling factors and final weight values in $\mathbf{W}_p$ are stored for alignment of new batches. Variable 5 (reactor contents volume change) contributed the most to $\mathbf{W}_p$ in this case study since its profile resembles the time axis more than the other variables.

MPCA for SPM

PCA techniques are used to develop a model describing the expected variation in process variables under NO. Principal Components (PCs) are a new set of coordinates that are orthogonal to each other. PCA involves the orthogonal decomposition of process variables data $\mathbf{X}$ along the directions that explain the maximum variation

in the data. These directions are the eigenvectors $\mathbf{p}_a$ of $\mathbf{X}^T\mathbf{X}$ or the PC loadings. The eigenvalues define the corresponding amount of variance explained by each eigenvector. The score matrix, $\mathbf{T} = \mathbf{XP}$ provides the coordinates with respect to these PC directions. Decompose the mean-centered and scaled $K \times J$ data matrix $\mathbf{X}$

$$\mathbf{X} = \mathbf{TP}^T + \mathbf{E} \quad \text{or} \quad \mathbf{X} = \mathbf{t}_1\mathbf{p}_1^T + \mathbf{t}_2\mathbf{p}_2^T + \ldots + \mathbf{t}_A\mathbf{p}_A^T + \mathbf{E} \tag{1}$$

where $\mathbf{P}$ is $J \times A$ whose ath column is the ath eigenvector of $\mathbf{X}^T\mathbf{X}$, $\mathbf{T}$ is a $K \times A$ score matrix, and $\mathbf{E}$ is the $K \times J$ matrix of residuals. A is chosen such that there is no significant process information left in $\mathbf{E}$.

MPCA decomposes $\mathbf{X_v}$ or $\mathbf{X_b}$ (Fig. 1b and c, respectively) into scores $\mathbf{t}_a$ and loading vectors $\mathbf{p}_a$. When MPCA is applied to aligned $\mathbf{X_v}$, estimation of future portions of variable trajectories is not needed because $\mathbf{P}$ is $(J \times A)$. However, if MPCA is applied to $\mathbf{X_b}$, $\mathbf{P}$ is $(KJ \times A)$ which requires the full $(1 \times KJ)$ measurements vector $\mathbf{x}_{\text{new}}$ while only $(1 \times kJ)$ of $\mathbf{x}_{\text{new}}$ is available at time k. MPCA on $\mathbf{X_v}$ is used in this study for online monitoring:

$$\hat{\mathbf{t}}_k = \mathbf{x}_{\text{new, dtw}}\mathbf{P}, \qquad \mathbf{e}_k = \mathbf{x}_{\text{new, dtw}} - \hat{\mathbf{t}}\mathbf{P}^T \tag{2}$$

where $\hat{\mathbf{t}}_k(1 \times A)$ denotes estimated scores and $\mathbf{e}_k(1 \times J)$ residuals calculated when a new $\mathbf{x}_{\text{new}}$ becomes available at each time k. The online MV DTW algorithm is applied prior to calculations in Eq. (2) to obtain the aligned measurements vector $\mathbf{x}_{\text{new, dtw}}$.

MPLS for Quality Prediction

MPLS algorithm uses $\mathbf{X_b}$ $(I \times KJ)$ and $\mathbf{Y}$ $(I \times M)$.[8] $\mathbf{X_b}$ is mean-centered to remove the nonlinear dynamic behavior of variable trajectories and usually scaled to unit variance. An MPLS model of NO with A latent variables is developed between $\mathbf{X_b}$ and $\mathbf{Y}$ collected from 'good' batches by decomposing $\mathbf{X}$ and $\mathbf{Y}$ into a combination of scores $\mathbf{T}(I \times A)$, loadings $\mathbf{P}(KJ \times A)$ and $\mathbf{Q}(M \times A)$, weights $\mathbf{W}(KJ \times A)$, and residual matrices $\mathbf{E}(I \times KJ)$ and $\mathbf{F}(I \times M)$ such that

$$\mathbf{X_b} = \mathbf{TP}^T + \mathbf{E}, \qquad \mathbf{Y} = \mathbf{TQ}^T + \mathbf{F}. \tag{3}$$

The data matrix $\mathbf{X}_{\text{new}}(K \times J)$ of a finished batch run is unfolded and scaled to $\mathbf{x}_{\text{new}}$ $(1 \times KJ)$ to predict scores $\hat{\mathbf{t}}(1 \times A)$, quality variables $\hat{\mathbf{y}}(1 \times M)$ and residuals $(\mathbf{e}, \mathbf{f})$

$$\hat{\mathbf{t}} = \mathbf{x}_{\text{new}}\mathbf{W}(\mathbf{P}^T\mathbf{W})^{-1}, \qquad \hat{\mathbf{y}} = \hat{\mathbf{t}}\mathbf{Q}^T, \qquad \mathbf{e} = \mathbf{x}_{\text{new}} - \hat{\mathbf{t}}\mathbf{P}^T, \qquad \mathbf{f} = \mathbf{y}_{\text{new}} - \hat{\mathbf{y}} \quad (4)$$

to compare with those of reference batches. At pre-scheduled intervals such as $k = 50, 100, \ldots, ki, \ldots, K$, aligned reference process measurements in $\mathbf{X}_{\mathbf{v}}$ are arranged into augmented $\mathbf{X}_{\mathbf{bi}}$ matrices $(= [\mathbf{X}_{\mathbf{b1}}; \mathbf{X}_{\mathbf{b2}}; \cdots; \mathbf{X}_{\mathbf{b}}])$ and a number of MPLS models are developed as described in Eq. (3) between these matrices and $\mathbf{Y}$ containing final quality variables of reference batches (Fig. 1c). These models provide early predictions of final product quality at the scheduled intervals.

MV charts and their control limits

Score plots of latent variables are used to detect departures from the in-control region defined by control (confidence) limits calculated from the reference set. Control limits for scores are computed using Student's t-distribution assuming that scores $\hat{\mathbf{t}}_k$ have Normal distribution [24]:

$$\hat{\mathbf{t}}_k \pm t_{K-1,\alpha/2}\mathbf{s}_{\text{ref,k}}(1 + 1/K)^{1/2}, \quad (5)$$

where $t_{K-1,\alpha/2}$ is the critical value of Student's t with K-1 degrees of freedom at significance level $\alpha/2$, K and $\mathbf{s}_{\text{ref,k}}$ are the number of observations and the estimated standard deviations vector, respectively, of $\hat{\mathbf{t}}_k$ at time k.

T^2 *chart* detects small shifts and deviations from normal operation defined by the model. T^2 and its statistical limits are also calculated by using the mean-centered score matrix. T^2 values at each time k follow an F-distribution [25]

$$T_k^2 = \hat{\mathbf{t}}_{\text{new},k}^T\mathbf{S}_k^{-1}\hat{\mathbf{t}}_{\text{new},k}\frac{I(I-A)}{A(I^2-1)} \quad \sim F(A, I-A) \quad (6)$$

where $\hat{\mathbf{t}}_{\text{new},k}$ is the predicted score vector of the new batch calculated using Eq. (4), I the number of reference batches, A the number of latent variables (or PCs) retained in the model, and $\mathbf{S}_k = \hat{\mathbf{t}}_k^T\hat{\mathbf{t}}_k/(I-1)$, the covariance matrix of $\hat{\mathbf{t}}_k$ at time k.

The *squared prediction error* (SPE) chart shows large variations and deviations from normal operation that are not defined by the model. SPE values calculated over J variables at time k using Eq. (4) are well approximated by χ^2 distribution

$$\mathrm{SPE}_k = \sum_{j=1}^{J} e_{jk}^2 \quad \sim g\chi_h^2 \tag{7}$$

where g is a constant and h is the effective degrees of freedom of χ^2. [26]

Contribution plots for fault diagnosis

Contribution plots for T^2, SPE, and scores show which variable(s) are responsible for inflating T^2, SPE or scores to indicate deviation from NO. Recently, control limits have been suggested for contribution plots.[21,28] These limits are adapted in this work for contributions to T^2 and SPE. Contributions to SPE can be calculated by [27,28]

$$C_{\mathrm{SPE},ijk} = e_{ijk}^2, \tag{8}$$

where $C_{\mathrm{SPE},ijk}$ is the contribution of batch i to the SPE value for process variable j at time k. Variable contributions to T^2 and scores can also be calculated as [29]

$$C_{T_k^2,j} = \sum_{r=1}^{R} \mathbf{S}_{rr}^{-1} t_{\mathrm{new},r_k} \mathbf{x}_{\mathrm{new},jk} p_{r,j}. \tag{9}$$

Online implementation procedure

New data $\mathbf{x}_{\mathrm{new}}$ $(1 \times J)$ is monitored by using the following algorithm for each sampling point k and quality predictions at each pre-scheduled point $k = k1, k2, \ldots, ki, \ldots, K$. For $k = 1 \ldots K$

1. Acquire new batch data vector: $\mathbf{x}_{\mathrm{new}}$ $(1 \times J)$
2. Find the most similar points in reference set trajectories by performing MV DTW to obtain aligned measurements vector $\mathbf{x}_{\mathrm{new,\,dtw}}$
3. Calculate new batch scores, SPE, T^2 and variable contributions to these statistics by using the MPCA model parameters (Eq. 2)
4. If $k = ki$ then arrange aligned process measurements $\mathbf{x}_{\mathrm{new,\,dtw}}(ki \times J)$ into $\mathbf{x}_{\mathrm{bki}}(1 \times kiJ)$ to obtain final quality predictions
5. Check MV control charts for abnormalities.

Table 1. Process and product quality variables of simulated PVAc process[30]

	Process Variables (* = inputs)		Quality Variables
1	Monomer volume fraction	y_1	Conversion
2	Solvent volume fraction	y_2	Polydispersity
3	Initiator concentration	y_3	Number average MW
4	Reactor temperature	y_4	Weight average MW
5	Reactor contents volume		
6	Coolant temperature *		(MW = Molecular weight)
7	Feed temperature *		
8	Feed initiator concentration *		
9	Feed flow rate *		
10	Feed solvent volume fraction *		

Case Study: Monitoring of Polyvinyl Acetate Polymerization

The model of free-radical solution polymerization of vinyl acetate in a fed-batch stirred reactor,[30–32] consists of 5 ordinary differential equations for reactor temperature, reactor contents volume, solvent volume fraction, monomer volume fraction, and initiator concentration in the reactor, and 3 differential equations for the moments of molecular weight distribution. Table 1 lists process and quality variables used. The monitored variables are assumed to be recorded at one minute intervals, though polydispersity measurement in a physical system may take up to 30 minutes.

The reactor is initially operated in fed-batch mode with a constant feed flow rate, then switched to batch operation when the desired reactor volume is reached. The initial reactor contents volume is set to 1 L to avoid a singularity in computations when $V = 0$. Small changes in feed conditions are simulated via a pseudo random binary signal (PRBS), resulting in low magnitude reactor dynamics. Random fluctuations in inputs, especially the feed flow rate, determine the length of the fed-batch phase, since volume determines the switching time. NO data are collected for model development

from simulations. To map the parameter space for NO model development, initial conditions are randomized within preset limits. The overall heat transfer coefficient of the cooling jacket and the initiator efficiency are also randomized. Average values of final quality variables are computed from the reference set and desired specification ranges are assigned using these averages as $\pm 1\%$ for y_1 and $\pm 5\%$ for $y_2 - y_4$.

Online Monitoring and Quality Prediction

Data from 30 batch runs are used as reference data set for model development. Since each batch has a different completion time and data length, data equalization and alignment is required prior to modeling. Data alignment is performed by DTW because there are no suitable indicator variables that could have provided a simpler alignment technique. After alignment, all batches have equal number of data points ($K = 425$). An MPCA model is developed using $\mathbf{X_v}$ ($IK \times J$) for online monitoring of new batches. 4 PCs are selected by using the broken stick method.[12] For end-of-batch quality prediction, $\mathbf{X_v}$ ($IK \times J$) is rearranged into $\mathbf{X_b}$ ($I \times KJ$) and partitioned into 9 matrices at each 50 increment of data with respect to time ($k1 = 50, k2 = 100, \ldots$). 9 different MPLS models are developed between partial process variables matrix $\mathbf{X_{bi}}$ ($I \times kiJ$) and $\mathbf{Y}$ ($I \times M$) for online quality prediction.

Illustrative Cases

Two fault cases, a pulse in coolant temperature and a drift in feed flow rate, illustrate the monitoring and quality prediction methods described. The process is assumed out-of-control if three consecutive points are outside 99 % confidence limit.

Case 1. A pulse change of magnitude 2 % is introduced in coolant temperature between time points 100 and 200. SPE detected the fault faster than T^2 (Fig. 2a and b). Score plots of PCs 1 and 4 also detect the fault (Fig. 2e and h). Variable contributions to SPE and T^2 are inspected (Fig. 2c and d). $C_{SPE,100-150}$ denotes the contribution of each process variable to SPE in time interval 100-150. Variable contributions to SPE identify the source of deviation as variable 6, coolant temperature, successfully.

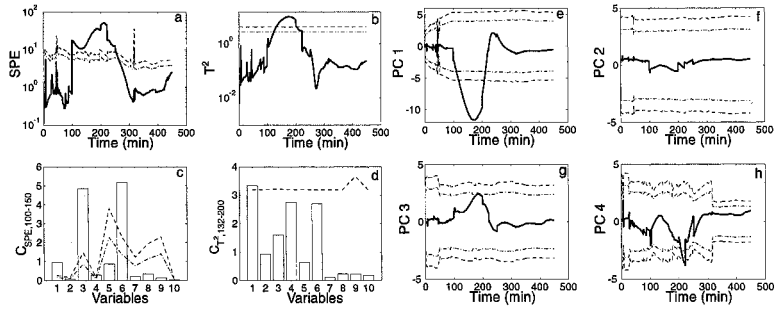

Figure 2. Control charts for SPE and T^2 (a, b). Contributions of variables to SPE and T^2 for a selected interval after the batch is out-of-control (c, d). Score plots (e–h). 95% and 99% control limits (dashed-dotted and dashed lines).

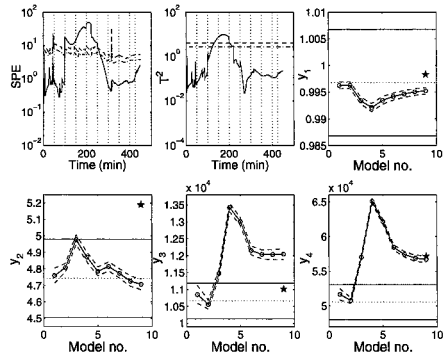

Figure 3. Case 1 online predictions for end-of-batch quality variables (○). Mean values of variables: center dotted line (upper and lower desired specifications: solid lines), confidence limits: upper and lower dashed lines., and actual final product quality (⋆).

They also identify the affected variables 1 (monomer volume fraction), 3 (initiator concentration) and 4 (reactor temperature). For T^2 variable contributions variable 1 is the only variable with significant contributions. Local modeling results show the deviation in product quality variables ($y_2 - y_4$) by the third model (Fig. 3). Although the fault is corrected after the 4th model, the degradation in final product quality (y_4) at the end of the run can not be prevented.

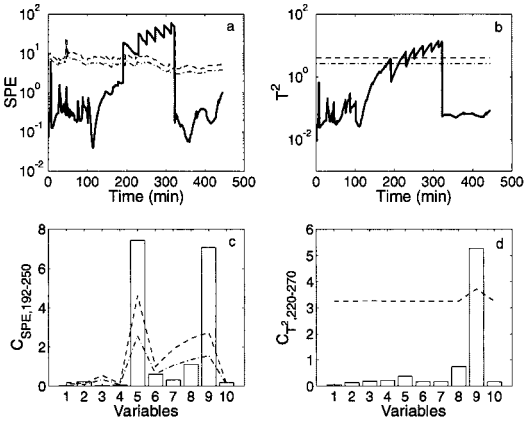

Figure 4. Case 2 Control charts for SPE, and T^2 (a, b). Contributions of variables to SPE and T^2 for selected intervals after out-of-control signal. 95% and 99% control limits (dashed-dotted and dashed lines).

Case 2. A drift of magnitude -2 % is introduced in feed flow rate at 100 min until the end of batch. An upward trend starts after 100 min in both SPE and T^2 plots (Fig. 4a and b). SPE exceeds 99 % out-of-control limit 28 minutes earlier than T^2. Only the scores plot of PC 4 detected the fault. Although the fault is not corrected, the process corrects itself after going to batch phase from fed-batch phase since there is no feed flow in the batch phase. Variable contributions to both SPE and T^2 identify the source of deviation as feed flow rate (variable 9) (Fig. 4c and d). SPE contributions also identify the affected variables solvent volume fraction (variable 2) and reactor contents volume (variable 5).

Product quality plots start to deviate from average quality values in the reference set when SPE and T^2 plots go out-of-control (Fig. 5). After some time they converge to the average values with a good prediction of the final product quality values. Although a fault was introduced into the process, final product quality is not affected.

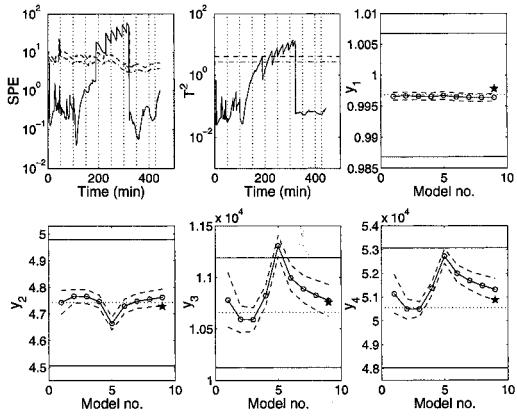

Figure 5. Case 2 online predictions for end-of-batch quality variables (○). Mean values of variables: center dotted line (upper and lower desired specifications: solid lines), confidence limits: upper and lower dashed lines, and actual final product quality (⋆).

Conclusions

An integrated MSPM framework is presented for online performance monitoring and fault diagnosis of batch polymerization processes. Unfolding the three-way data array by preserving variable direction allows online monitoring without requiring future value estimation. Alignment of variable trajectories and online quality prediction are integrated into MSPM. Predicting end-of-batch quality during the progress of a batch provides useful insight to anticipate the effects of excursions from normal operation on final quality. Statistical limits on contribution plots enhance identification of variables that contribute to the inflation of SPM statistics and improve the diagnosis capabilities.

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