Correlating Polymer Resin and End-Use Properties to Molecular-Weight Distribution

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The prediction of polymer resin and end-use properties for a dual-reactor solution polyethylene process is investigated. Polymer molecular-weight distribution (MWD) is highly influential in achieving the desired properties, but the extent of the importance and key areas of distribution to achieve specific properties are less well understood. The best empirical approach for resin and end-use property prediction using the entire MWD along with other influential variables as inputs is investigated. Two modeling methods are considered: partial least squares (PLS) and a novel strategy that uses the weight fraction of polymer in a given molecular-weight range (referred to as a binning technique). Both linear and nonlinear variants of the two algorithms are used. The intention is to develop a model that facilitates the analysis of the simultaneous influences of process operating conditions and resin characteristics such as MWD on a specified set of end-use properties. Results demonstrate that the nonlinear variant of the binning technique provides the highest accuracy as well as indicating regions of MWD that are of greatest influence. Such information is particularly useful for the control of the polymerization reactors.

Introduction

When producing polyethylene, the properties must be tailored toward the end use of the product. For instance, a film would require a polymer that is tough and flexible. Injection-moulding operations require polymers characterized by rigidity, but possessing good flow properties. Plastic pipes require strength, and wire insulation requires good processing characteristics with resistance to stress cracking (Billmeyer, 1984).

It is known that these properties are affected by a number of factors, with molecular structure being one of the most important. Molecular structure refers to molecular-weight distribution (MWD) and the parameters that describe it, namely weight-average molecular weight ($\overline{Mw}$), number-average molecular weight ($\overline{Mn}$), polydispersity index ($\overline{Mw}/\overline{Mn}$) and so on. The interrelationship between density, melt index (MI), and $\overline{Mw}/\overline{Mn}$ in producing polymers with desirable end-use properties was discussed in McGrew (1958). Many industrial strategies are still configured to regulate MI, density, and aspects of the MWD (Lines et al., 1993) rather than directly controlling details of the MWD that relate to end-use property specification.

Recently, work concerning the prediction of polymer resin and end-use properties has started to appear. For example, Ohshima and Tanigaki (2000) contrasted models with empirical structure specified using qualitative insight with a wavenet-based neural network to predict the MI of the polymer. Latado et al. (2001) developed empirical models to predict polymer end-use properties as functions of fundamental molecular and morphological properties (such as $\overline{Mw}$, polymer composition, degree of crystallinity). They demonstrated using measured process data so that accurate empirical models could be obtained. However, these property correlations were based upon measured process operating conditions and/or the parameters that describe MWD, and not the actual distribution. Ariawan et al. (2001) demonstrated that it is often more useful to consider the whole of the MWD curve when correlating the effect of molecular structure to the rhe-

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ology of the polymer. This is especially true when the MWD is skewed. Often extra concentrations of molecules in the high- or low-end regions of the MWD can result in significantly different rheological and processing behaviors. In Ariawan et al. (2001) it was found that extensional and elastic properties of the resins were dependent on the concentration of larger molecules, and in particular, on the tails in MWD at the high end.

Our objective is to demonstrate that through the use of the entire MWD along with other structural characteristics, such as comonomer incorporation, accurate resin and end-use property predictions can be obtained. One resin and two end-use properties are estimated, MI, shear thinning ratio (STR), and Dart Impact. It is known that MI provides a relatively trivial example for single reactors; however, with a dual-reactor configuration, the correlation of MI to $\overline{Mw}$ is weaker and the prediction is not as straightforward. STR and Dart Impact were selected because they are important quality indicators, and they provide a more difficult example for both single- and dual-reactor configurations.

Because of the lack of theoretical knowledge regarding the relationship between resin structure and end-use properties, two empirical modeling methods are considered: partial least squares (PLS) and a novel strategy that uses the weight fraction of polymer in a given molecular-weight range (referred to as a binning technique). Both linear and nonlinear variants of the two algorithms are used. The intention is to develop regression models that facilitate the analysis of the simultaneous influences of resin processing conditions and resin structure (MWD) on a specified set of end-use properties. By better understanding the relationship between resin structure and end-use properties, process control can be better focused on aspects of the resin structure that are critical to a particular resin grade, thus leading to a more consistent product.

Process Description

The polyethylene process is a solution polyolefin technology. The process consists of two reactors in series (see Figure 1). The reactor system can be configured and operated differently so as to obtain specific resin characteristics. Ethylene and comonomer are fed to the first reactor, as is the catalyst and hydrogen. Product from the first reactor is fed to the second reactor along with a second feed stream of ethylene, comonomer, catalyst, and hydrogen. The feeds to each reactor can be controlled independently, which provides flexibility to tailor resin properties. The reactors are operated at moderately high temperatures and high pressures. Process disturbances arise because of impurities in the feeds and variations in catalyst quality.

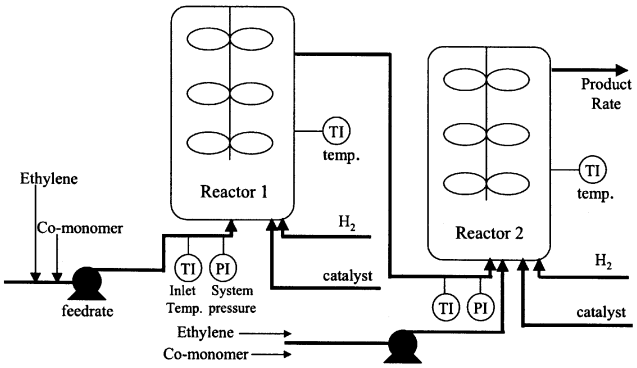

Figure 1. Polyethylene production process.

Traditionally resin properties that are controlled are melt index (MI or I_2), density, and a measure of the breadth of the MWD. However, given the flexibility in a dual-reactor process to tailor the distributional properties of the resin, these may no longer be sufficient. The development of on-line sensors could improve the situation by making additional information available in real time. These would be complemented by the use of a mathematical model to predict difficult-to-measure process variables.

Using the MWD to predict end-use properties

Figure 2 shows typical MWDs from the dual-reactor process and the associated variation in end-use properties. The MWD is measured by using gel permeation chromatography (GPC), and the trace is the weight fraction of polymer produced with a given molecular weight (MW) as a function of $\log_{10}$(MW). MI was measured in accordance with the ASTM D1238 norm, which documents measurement errors of 5–11% for the MI range in question.

STR is the ratio of polymer melt viscosity at 10 and 1,000 s^{-1}, and is subject to errors of approximately $\pm 5\%$. Dart Impact was measured using ASTM D1709/A, and is subject to a standard error of $\pm 10\%$ for repeat measurements on the same sample. When errors introduced by variations in film blowing conditions are considered, a total error in Dart Impact of $\pm 25\%$ or more is not an unreasonable estimate.

The data shown in Figure 2 highlight some important features. First, it can be seen that the MWD is subject to subtle changes in mean and width that lead to variations in the resin and end-use properties. The reactors have been operated to produce MI and STR generally in the low range, but a limited number of higher values were obtained. Second, a wide variation in Dart Impact can be observed. As previously mentioned, Dart Impact is subject to errors in both the Dart measurement itself and the film-blowing conditions, and so a larger spread of information is to be expected. The high frequency of 1,000-g Dart Impact values is an artefact of the testing. Since a value of 1,000 g is sufficient for many film applications, testing was stopped at a value of 1,000 g for some of the samples and these need to be excluded in further analysis.

MI prediction was considered for both the single- and dual-reactor situations. For the single-reactor case, 46 samples were available, whereas there were 101 samples for the dual-reactor case. STR and Dart Impact were only considered for the dual-reactor configuration with again 101 samples available.

Empirical modeling methods

Because the MWD is multivariate, an obvious approach to empirical model development is to use a multivariate technique such as partial least squares (PLS) to develop a relationship between the MWD and end-use properties. In addition, however, rather than attempting to capture product quality characteristics by weighting the various elements that

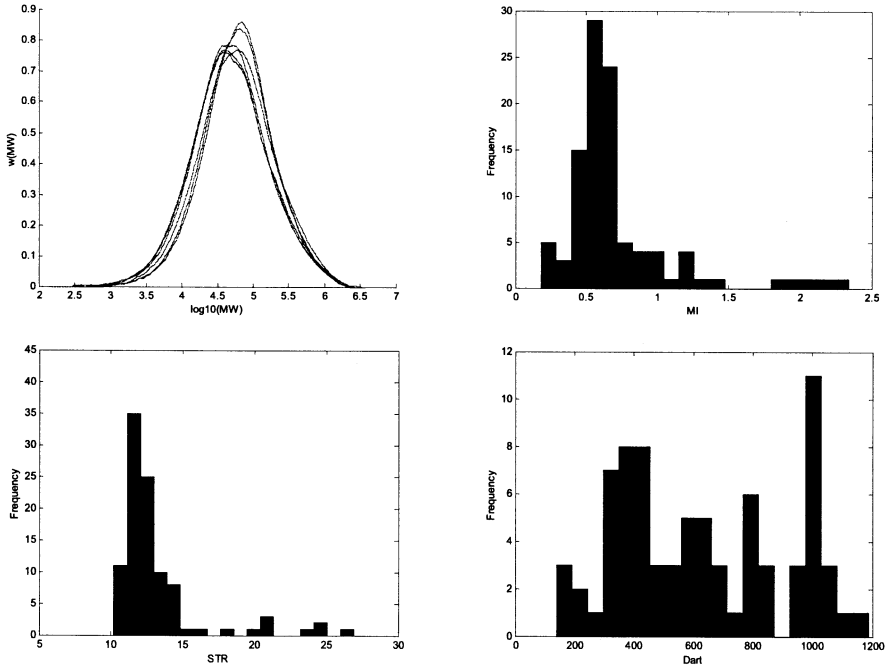

Figure 2. Extent of end-use property variation and the associated MWD (dual reactor).

make up the whole distribution (as in PLS), only critical areas of the distribution may be used. This would involve applying qualitative understanding of polymer resin and end-use properties and estimating their relationship to certain molecular weights within the MWD. The potential of this method is that relevant areas of the MWD for each individual resin and end-use property can be identified, which should ultimately improve process monitoring and control. Since it is not known in advance whether linear or nonlinear strategies will be required, both are considered.

1. *Partial Least Squares*. PLS is a linear multivariate modeling procedure that has achieved widespread use in the fields of chemometrics and process monitoring. The algorithm operates by projecting input-output data onto a number of orthogonal latent variables and then modeling the relationship between these new variables (the so-called inner models) by univariate linear regression.

The main advantages of the technique are summarized as follows:

- As a result of projecting the inputs and outputs onto a lower-dimensional space, the algorithm is robust to measurement noise;
- Because the algorithm calculates latent variables sequentially and only performs univariate regressions at each stage, problems associated with modeling colinear (correlated) data are removed;
- By reducing the dimensionality of the relationship between the input and the output space and selecting latent variables that maximize the covariance between the input and the output space, the algorithm facilitates visualization of the relationships within the data set.

There have been a number of successful applications of PLS to process systems reported in the literature. For instance, MacGregor et al. (1994) provide an overview of multivariate projection methods and use PLS for the modeling of a polyethylene reactor, which is subsequently used for monitoring and fault detection. MacGregor and Kourti (1995) provide a more detailed tutorial of these techniques, applied to an industrial polymerization process. Gallagher et al. (1996) also present a good review of the technique with application to a nuclear-waste-vitrification process. PLS has been used by several researchers for the analysis of distributions. The normal objective is to correlate distribution information to product quality parameters. For instance, Harthun et al. (1997) applied PLS to NIR spectrum to analyze for protein concentration in a bioreactor. Lee and Chung (1998) used NIR spectroscopy for the rapid and nondestructive analysis of ethylene content in flake and pellet propylene/ethylene copolymer. Using PLS combined with a second derivative algorithm, relevant spectral information was successfully extracted and correlated with a conventional infrared (IR) method. Seasholtz (1999) presents four case studies on the application of NIR and NMR spectroscopy. Chemometric methods used included multivariate calibration with PLS and pattern recognition.

2. *Using the Weight Fraction of Polymer in a Given Molecular-Weight Range* (*the binning method*). From a fundamental process understanding, it is thought that relative proportions of the polymer between particular molecular weights have an influence on polymer resin and end-use properties. For example, MI is primarily influenced by higher molecular weights because MI is being measured at a low shear rate. However, in the case of STR it would be expected that it would be influenced by both high and low molecular weights, as it is a ratio of viscosity at a low shear rate to that at a high shear rate. Unfortunately, it is not known exactly which points on the MWD should be considered. However, these points could be determined using a two-tier optimization approach.

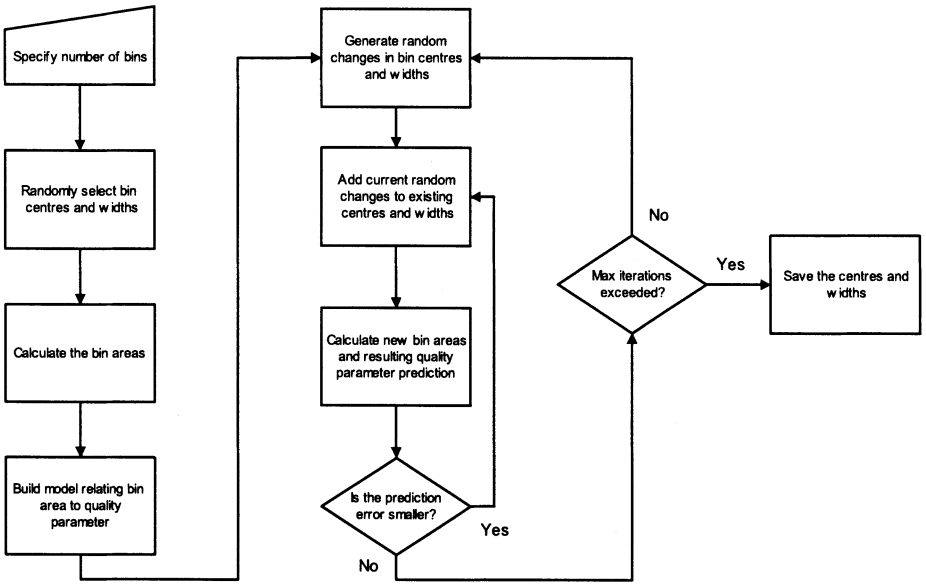

Figure 3. Linear bins program flow chart.

The first stage would determine which points on the MWD should be considered. As w(MW) represents the point on a continuous distribution, the area under the curve is given by (see Figure 4)

$$A_1(\log_{10} MW) = \int_{P_{11}}^{P_{12}} w(MW)\, d\log_{10} MW$$

Since the relative proportions of the polymer between certain molecular weights (P_{11} to P_{12}) influence the physical properties, the differences in area from one "bin" to the next could be used as an indicator of variations in resin and end-use properties. While it may be possible to correlate a single bin to the end-use property in situations where the breadth of the MWD is constant, for the dual-reactor operation, the MWD made in each reactor can be changed to deliberately change the breadth of the overall distribution. Since the breadth is no longer constant, more than one bin may be required to predict the end-use polymer property. Consequently, n bin areas, $A_1,\ldots,A_n$ are considered (where the value of n is determined so as to obtain a minimum prediction error). Two parameters are used in order to obtain the bin areas: the bin center and width. This then allows the calculation of the appropriate areas, $A_1,\ldots,A_n$. The second stage of the procedure then builds a regression model between the bin areas and the end-use parameter (Q). The linear model is of the form

$$Q = \alpha_1 A_1 + \alpha_2 A_2 + \cdots + \alpha_n A_n + \alpha_{n+1}$$

where the coefficients are determined using a robust batch least-square procedure. The algorithm then iterates, repeatedly generating new bin areas and building models relating the areas to end-use property in order to minimize prediction error. The structure of the algorithm is summarized in Figure 3.

To initialize the algorithm, the number of bins must be specified. Typically, a maximum of four bins is used. Random bin center and width increments are generated from a normal distribution, with a standard deviation chosen to allow reasonable movement of the bin locations. If this is set too small, movement toward the optimal centers and widths will be prevented, as the algorithm has a greater potential to become trapped in a local minimum. If it is too large, then the number of iterations to arrive at a solution increases, though the potential of being trapped is reduced. Consequently, larger increments are chosen to ensure a better solution, albeit at the expense of increased computational effort. To terminate the algorithm the maximum number of iterations must be specified, and this is easily achieved through observation of training progress.

The final model structure is shown in Figure 4. In this case it can be seen that two bin areas are determined (coupled with a bias) to produce indicators of resin and end-use properties. In a modeling exercise it may be sufficient to relate

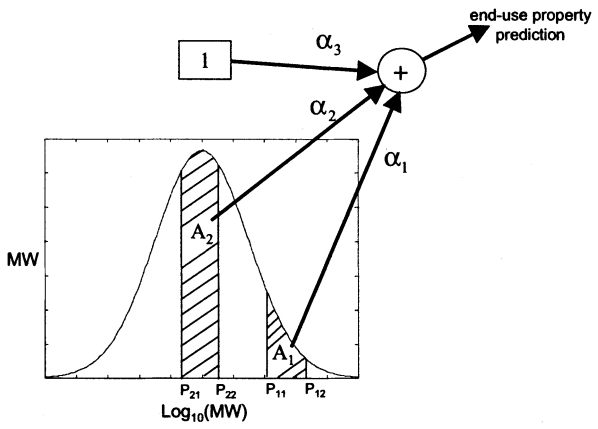

Figure 4. Bin model structure.

the bin areas to end-use properties, but depending upon the property under consideration, it could be necessary to augment these data with information on other resin characteristics, such as comonomer incorporation, or processing conditions.

3. *Nonlinear Techniques*. The modeling strategies just discussed build linear-regression models. If there is a known nonlinear relationship, nonlinear transformation of the polymer resin and end-use property could be considered (such as taking the log of MI is an accepted transformation); however, the model will still be "linear in the parameters." Alternatively, a nonlinear modeling method can be adopted.

(*a*) *Nonlinear PLS*. Nonlinear functions can be used to generate nonlinear variants of the PLS algorithm. For example, in Wold et al. (1989) the inner relationships were modeled using polynomials, while Qin and McAvoy (1992) proposed the use of feedforward artificial neural networks (FANNs) to model the inner relationships in PLS. It is the Qin and McAvoy (1992) approach that is used in this work, where FANNs with a single hidden layer of hyperbolic tangent activation functions are used to generate the predictions. The main reason for choosing this network structure is that FANNs are the most common architecture employed and a single hidden layer of hyperbolic tangent activation functions is sufficient for modeling purposes. There is no evidence to suggest that for example radial basis function networks would not provide the same degree of accuracy in model predictions.

(*b*) *Nonlinear Bins*. The approach used to build the nonlinear bin models was to use a FANN instead of a linear model to relate bin areas to end-use property data. A potential drawback of this strategy is that the training of the network is an iterative procedure, as is the bin specification. A rigorous strategy would therefore involve the training of a FANN for each iteration of the bin algorithm to find both the optimum bin centers and widths as well as network weights. As this would involve excessive computation, a compromise was adopted by utilizing the same ideas adopted by Wold et al. (1989) in the formulation of the "quick and dirty" PLS algorithm. Thus, it is assumed that the bins determined from the linear model are the same as those that should be adopted for the nonlinear model (with quick-and-dirty PLS, the linear latent variable projections are used with nonlinear inner models). This may compromise the quality of the relationships developed, as the ideal bin positions are not necessarily the same for the linear and nonlinear algorithms, and may lead to a suboptimal solution. However, while being suboptimal, this should give an indication of whether benefits would be found by adopting the nonlinear model structure.

Experimental method

Because the training of FANNs can be affected by the random initialization of network weights, and because there will be variation in the bin initialization as well as their random modifications to find optimum positions and width, results will vary from one run to the next. Multiple runs must therefore be performed in order to give a more accurate indication of the performance of each algorithm. In this work, sets of one hundred algorithm runs were carried out for each of the systems studied. Although a greater number of runs may add greater statistical significance to the results, run time is also a consideration, and it was found that this number provided a reasonable compromise.

Before the sets of runs can be compared, the "best" model from each run must be selected. Since we are interested in developing models that have the ability to generalize (fit unseen data well), an additional set of data points was used for model testing. In all cases the samples were split into two portions, two-thirds for model construction and one-third for testing the quality of the resulting model.

Table 1. Rms Prediction Error of MI Using Measured Plant Data

	Single Reactor		Dual Reactor	
	Train	Test	Train	Test
$\overline{Mw}$ correlation	0.123	0.0956	0.1292	0.1056
Linear bins	0.091	0.059	0.196	0.122
Linear bins (log MI)	0.0456	0.0437	0.122	0.061
Nonlinear bins	0.0498	0.0432	0.059	0.0603
PLS (log MI)	0.0851	0.0558	0.208	0.0786
Nonlinear PLS	0.055	0.0969	0.117	0.0829

Prediction of Melt Index

The initial results based upon the MWD distributions are shown in Table 1. The $\overline{Mw}$ correlation relates weight-average molecular weight to MI, and the following relationship was obtained in the single-reactor case

$$\log_{10} MI = -3.7286 \log_{10}\left(\overline{Mw}\right) + 18.6851$$

This relationship is in keeping with results reported previously (Billmeyer, 1984) and provides an excellent comparison for the more complex techniques. All the other models use the measured MWD as input to predict the MI. Cross-validation was used to determine the optimal number of bins and latent vectors.

First, considering the bins results, it should be noted that the rms errors refer to the optimal number of bins. The optimal number of bins depends upon the reactor configuration. In both the single and dual cases, the training error decreases as the number of bins increases. However, Figure 5 shows the testing data error and clearly indicates an optimal number of bins as a result of overfitting when using an excessive number. These results refer to the prediction of the log transformed MI, which gives an improved prediction over the untransformed MI. A nonlinear relationship clearly existed and log transformation reduced the degree of nonlinearity resulting in a better fit.

Because MI is highly correlated to $\overline{Mw}$, it would be expected that one bin would be sufficient for single-reactor data, as the breadth of the distribution does not vary significantly. Furthermore, from a fundamental perspective the bin would appear on the higher side of the distribution. This bin was indeed consistently at the high end of the distribution. Figure 5b indicates that three bins gave the best model in the case of the dual reactor, as this has the lowest rms error, and it is this configuration that gives rise to the results in Table 1. With dual-reactor operation, the MWD made in each reactor

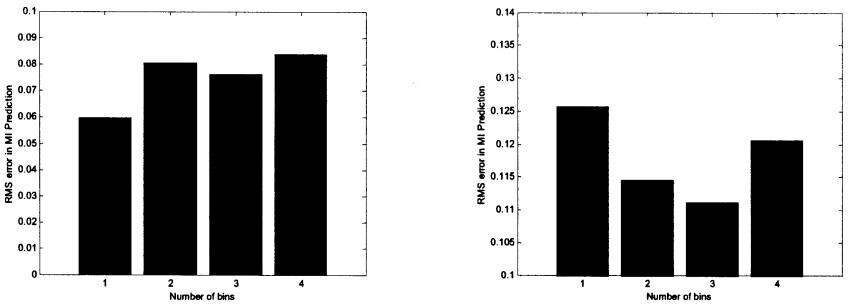

Figure 5. (a) Single- and (b) dual-reactor testing data.

can be changed to deliberately change the breadth of the overall distribution. Since the breadth is no longer constant, more than one bin is required to relate the MWD to the $\overline{Mw}$, and, hence, to MI.

Figure 6a and 6b show the position of the bins for the dual-reactor case when a model is generated to predict the log of MI. Figure 6a shows the top 25% of the results (judged on the testing set) when building the bins-based model 100 times, with the probability of selection being indicated. The reason for considering only a subset of the results is that poor models result if the bins become "stuck" in local minimum during the search process. It is clear that the bins are consistently located at the high molecular weight tail of the MWD, reinforcing the original speculation that this was indeed the influential area. Comparing the errors obtained between using one bin and three bins, it was observed that a 6% improvement in rms error was achieved, but it should be noted that the one bin prediction is also accurate. Figure 6b shows the MWs selected when three bins are used. Again the high molecular weight tail dominates the bin selection, but areas in the middle of the distribution are required to capture some of the more subtle variations in the MI.

Using the same cross-validation strategy, the optimal number of latent variables was selected for the PLS algorithm. Figure 7a shows that three latent variables provide the best solution. It is interesting to observe that while the bins method selects a narrow region of the MWD as being descriptive of changes in MI, PLS makes use of a significant proportion of the distribution. This is apparent in Figure 7b, where the normalized projection input weights for the three latent variables are shown. Because a significant proportion of the normalized weights used in the regression are nonzero, a considerable number of points that make up the MWD are being used for prediction.

The nonlinear variants of the binning and PLS algorithms were applied to the original MI data rather than the log-transformed values. The log transforms were taken because the linear methods could not cope with the system nonlinearity, but the nonlinear versions of the algorithm should not suffer from the same problem. It can be seen that for the case of the single reactor, the nonlinear bins method provides results with almost identical rms errors to that of the log-transformed MI bins. The only benefit arising from the nonlinear algorithm would be if an appropriate transformation for MI was not known. The results for the PLS algorithm demonstrate one of the pitfalls of using nonlinear models. In model construction, it is difficult to avoid problems such as overtraining and data extrapolation/interpolation, and this can potentially result in degradation in behavior beyond that experienced with a linear model. This seems to be true for the nonlinear PLS results, since the testing errors are higher than the training errors. While the same pitfalls could potentially affect the nonlinear bins algorithm, the testing and training errors are very similar. The focus of nonlinear bins

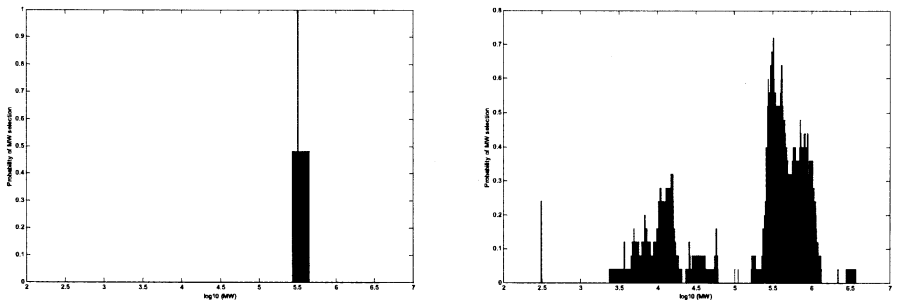

Figure 6. Bins position for the dual reactor case.

(a) Bin position with single bin (prediction of log MI) for dual-reactor case; (b) Bin position with three bins (prediction of log MI) for dual-reactor case.

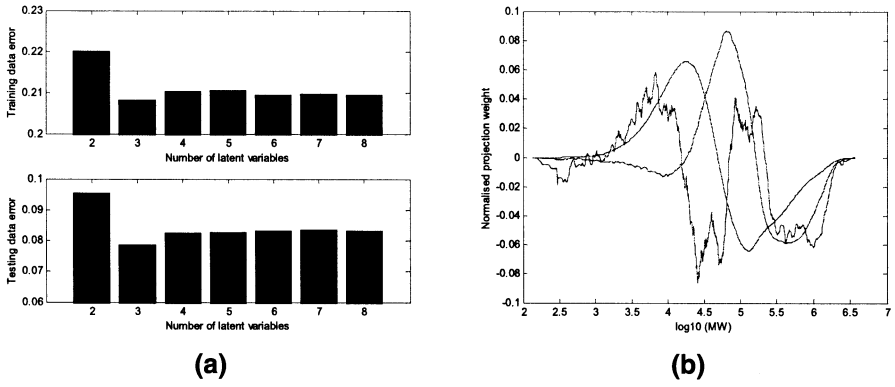

Figure 7. Latent variable selection and associated weights.

(a) Selection of the number of latent variables; (b) Normalized projection weights for the first three latent variables.

on a narrow, particularly descriptive range of the MWD, rather than the whole distribution, may be why it performs better on new data.

A direct comparison between dual- and single-reactor rms errors is not possible, as the distribution of data and operating regions are different, but it is clearly more of a challenge to extract information from the more complex distribution. The pattern of results between the methods is very similar to the dual-reactor case, that is, log-transformed MI and nonlinear bins are comparable, PLS results are less accurate, and the standard molecular-weight correlation provides a base case from which to compare improvements.

Figure 8a and 8b show the testing data results for the dual-reactor predictions of MI using the nonlinear bins and basic correlation methods.

Prediction of the shear thinning ratio

As with MI, the modeling techniques were applied to data from the dual reactor to predict STR. Table 2 shows the rms errors obtained. The procedures discussed earlier were used to determine model structure (that is, number of bins, number of latent variables). It can be seen that the nonlinear bins method provides the lowest rms error on both the training and validation data set.

Figure 9 shows the model accuracy obtained using the nonlinear bins. It can be seen that accurate predictions of STR are obtained on both the training and testing data over the whole range of values.

The probability of a particular molecular weight being selected for use within the nonlinear bins model is shown in Figure 10. It can be seen that as with MI, molecular-weight values toward the high end of the distribution are the most influential. Again values in the middle region of the distribution are needed to explain some of the more subtle variations in STR.

Prediction of Dart Impact

As with MI and STR, all modeling methods were applied to the dual-reactor and rms prediction errors generated. In the case of Dart Impact, the density (or comonomer content), in addition to the MWD, is key in predicting the performance of the resin, and so resin density was included as an additional input in all models. Table 3 summarizes the rms prediction errors obtained.

Figure 11a and 11b show the fit obtained using the nonlinear bins approach. End-use properties such as Dart Impact are designed to indicate the characteristics of the resulting polymer product material. It is, therefore, not only resin characteristics that are important to consider, but in making

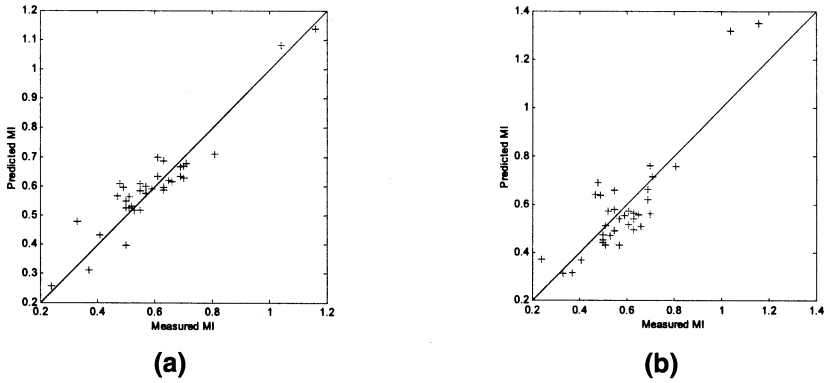

Figure 8. MI predictions for the (a) dual reactor with nonlinear bins, and (b) dual reactor with basic correlation.

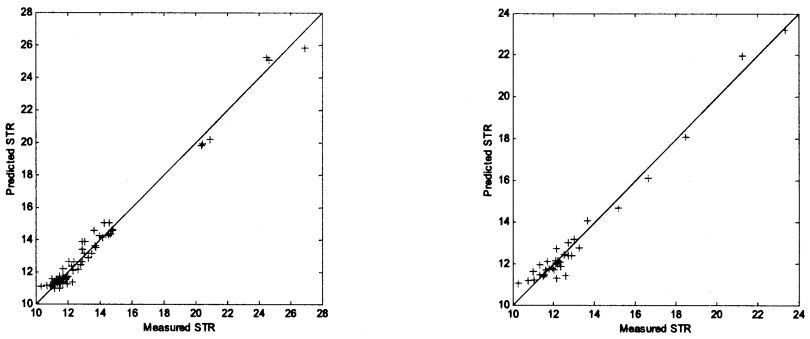

Figure 9. STR modeling with nonlinear bins method: (a) training data fit; (b) testing data fit.

comparisons between results, the method of sample production is also relevant. The Dart Impact tests for polymer produced in the dual reactor were carried out with two different extruders. The possibility of including an extruder-type indicator in the model was investigated, and the results were disappointing. Around 20% of the data were gathered with the first extruder. It was therefore decided to eliminate this information from the data set and accept that the model would only be applicable for the second extruder. Even when considering data generated using the second extruder, changes in extruder operating policy were implemented over the course of the data-gathering exercise. The extruder conditions were included as additional inputs for the Dart Impact model. In assessing the results it is also important to remember that Dart Impact is subject to considerable uncertainty. Total errors of $\pm 25\%$ or more are not unreasonable.

The models show that the majority of the variation in Dart Impact is explained by variations in resin density, with the rest explained by MWD and processing conditions. The probability of any particular molecular weight being selected for the nonlinear bins model is shown in Figure 12. It can be seen that in the case of Dart Impact prediction, three areas of the distribution are selected in the low, medium, and high molecular-weight regions. The implication of this is that differences in all regions of the distribution are essential if Dart Impact is to be predicted with any degree of accuracy.

Conclusions

This article has investigated MWD data-interpretation techniques for a dual-reactor polymerization process. MWD of a polymer is one of the more important quality-control variables in industrial processes, as end-use properties are dependent upon MWD. However, direct control of MWD is a difficult task. MWD is not measured on-line, and off-line indicators such as MI can be delayed by on the order of one hour. One solution is to improve on-line measurements; an alternative is to predict the MWD using a differential-equation model relating measured inputs to the distribution. Models such as the ones developed in this work can be used to identify key characteristics of the MWD, which can in turn be used to develop process-control strategies.

Neto and Pinto (2001) developed a steady-state model for slurry and bulk polypropylene polymerizations. The model was validated against actual process data and the regression relationships (linear, neural net) used in Latado et al. (2001) used to predict resin and end-use properties such as MI, the glass transition temperature, and the polymer impact resistance. The work described in this article is also part of a two-stage prediction strategy. The first stage uses a hybrid (mechanistic–neural network) model to predict MWD from reactor operating conditions. This article describes the second empirical stage that predicts resin and end-use properties using the predicted MWD from the hybrid model, as well as any necessary additional process measurements.

The hybrid model was developed in Hinchliffe et al. (2003) to accurately predict polyethylene process conditions, such as

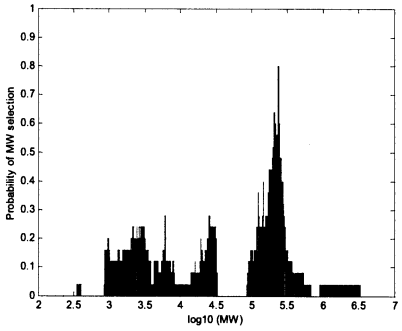

Figure 10. Bins position with three bins in the prediction of STR.

Table 2. Rms Errors for the Modeling of STR

	Bins		Nonlinear bins		PLS		Nonlinear PLS	
	Train	Test	Train	Test	Train	Test	Train	Test
STR	1.91	0.84	1.74	0.44	2.59	1.44	2.12	1.68

Table 3. Rms Errors for the Modeling of Dart Impact

	Bins		Nonlinear bins		PLS		Nonlinear PLS	
	Train	Test	Train	Test	Train	Test	Train	Test
Dart	129	195	96	143	154	218	219	272

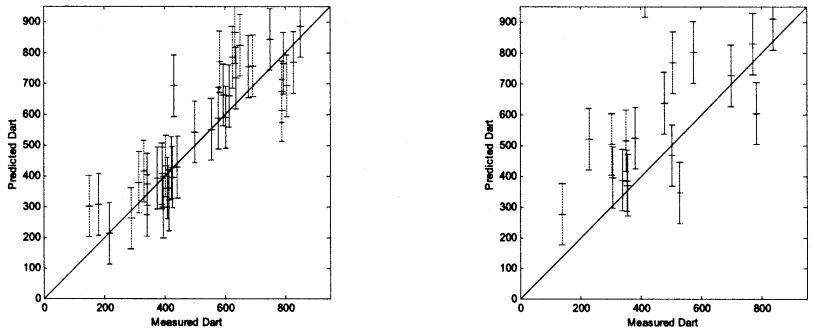

Figure 11. Dart modeling with nonlinear bins: (a) fit to training data; (b) fit to testing data.

the reactor temperatures and conversions along with resin characteristics such as MWD and comonomer incorporation. Because the neural network merely corrects key descriptors (states) that affect the calculation of the MWD, this stage maintains process understanding and portability essential for product-development studies as well as optimization of process operation. This article has demonstrated that MWD can be used to predict resin and end-use properties. Future work will utilize the hybrid model rather than the measured MWD to predict polymer end-use properties and consider how the overall scheme resides in a closed-loop control strategy. Whether closed-loop control through model-based methods is adopted or the use of the hybrid model in multivariate statistical process control (for example, Weighell et al., 2001) would be more suitable is under consideration.

Finally, we note that NIR spectra are normally calibrated to process quality using PLS. Some researchers report that calibration performance is dependent upon the spectral range used (for example, Chung et al., 1999). A number of variable selection/elimination methods have been proposed, including uninformative variable elimination and relevant component extraction (see Estienne et al. (2001) for a comparison of the methods). It would be interesting to compare the binning method described in this article with the alternative spectra calibration techniques. The method could be used as a separate procedure, or used as part of a hierarchical approach, the "binning" determining relevant areas of spectra coupled with PLS regression on the areas chosen.

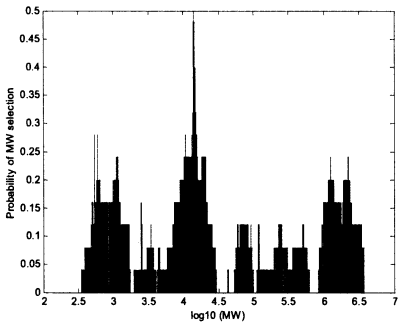

Figure 12. Bins position with three bins in the prediction of Dart Impact.

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