An Industry Perspective on Polymer Process Modeling

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Introduction

Many chemical engineers dedicate their careers to process and product development, process de-bottlenecking, and process optimization for manufacturing plants. As they perform process studies, whether it is related to hydrocarbons, petroleum, chemicals, or polymers, they often apply process modeling technologies and tools to capture and apply the fundamental engineering understanding of the industrial processes. These tools for process modeling generally offer chemical engineers a robust and easy-to-use environment to develop and apply process models both quickly and productively.

Process modeling technologies and tools evolved over the past 30 years. Initially these technologies were primarily developed to meet the needs of the hydrocarbon and petroleum industries. The technology was then gradually expanded to address the needs of the petrochemical industry and, later, processes involving synthetic fuels (Gallier et al., 1984) and aqueous electrolytes (Chen et al., 1983; Chen, 1987).

Innovations in process modeling technologies and tools for the polymer processes evolved recently. The feasibility of modeling polymer processes with general-purpose process simulators was questioned as late as the early 1990s. However, key innovations in various polymer process modeling technologies have emerged and made it possible to develop high fidelity polymer process models that can be used for process design and process optimization. As a result, the polymer industry has quickly and successfully adopted polymer process modeling technology.

This perspective highlights the unique challenges in polymer process modeling and the innovations that address these challenges. Also reported are the recent industrial applications of polymer process modeling technologies and tools that gradually came to wide acceptance in the past decade. Lastly opportunities for future innovations are suggested.

Challenges in Polymer Process Modeling

Until recently the use of process modeling technology in the polymer industry has been rare, and such activities were primarily handled by academic researchers or selected modeling "specialists" in centralized engineering organizations (Ko et al., 1992). When polymer modeling was required, the modeling scope was limited to the expertise domains of modeling "specialists," i.e., polymer reaction engineering and reactor modeling. When heat and mass balance calculations were needed for polymer processes, polymers would be approximated as heavy hydrocarbon in process simulators. Lack of experimental data and expertise in polymer thermodynamics further limited the value of early polymer modeling efforts. For example, when essential polymer reaction and reactor models were developed, phase equilibrium modeling was often grossly simplified or neglected. Consequently, these models offered only limited fidelity in describing and extrapolating behavior of industrial polymers, especially with multiple phase reaction systems. The value of these reactor models was further diminished as they could only be used by model-developers. The models could not be integrated into process simulators for process studies either.

Despite the fact that each polymer is unique and there was ubiquitous doubt as to whether a general-purpose polymer process simulator was even possible for modeling the wide variety of industrial polymers, much progress has been made with polymer process modeling tools in the past 10 years. Today, virtually all commercially important polymer processes have been successfully modeled with polymer process simulators. These process simulators provide innovative modeling functionalities to address key polymer modeling issues and challenges. Some of them are briefly discussed below.

- Polymer molecular structure: While it is essential that polymer process models perform heat and mass balances associated with conversion of monomers to polymers, the true value of polymer modeling lies with the ability to compute and track polymer quality in terms of polymer molecular structure attributes such as degree of polymerization, molecular weight distribution, polymer composition, branching frequency, sol and gel contents, etc. Some of these polymer molecular structure attributes are intensive variables such as degree of polymerization. Some of these attributes are extensive variables such as number of polymeric chains. Additional conservation equations or constitutive equations associated with these attributes must be solved for each process unit in order to compute and track these attributes throughout a process flowsheet.

- Polymerization reaction engineering: Polymer producers control polymer molecular structure primarily through the use of polymerization chemistries, catalysts, and reaction media. Examples are condensation polymerization, solution free radical polymerization, emulsion free radical polymerization, suspension free radical polymerization, ionic polymerization, addition polymerization with Ziegler-Natta catalysts or metallocene catalysts, etc. Polymer process simulators must provide polymerization kinetics models for commonly used polymerization systems and additional model interfaces to user reaction kinetics models or reactor models (Hungenberg et al., 2001). These polymerization kinetics models compute and track reaction rates, molecular weight distribution, particle size distribution, etc.

- Phase equilibrium: While polymerization chemistries control the reaction mechanism, for multiple phase reaction systems, it is the phase equilibrium of polymer solutions that determines the reaction media compositions that control the polymerization reaction rates and the resulting polymer molecular structure (Bokis et al., 1999). Process modeling tools must incorporate predictive polymer thermodynamic models and supporting flash algorithms for phase equilibrium to capture the phase behavior of the reacting polymer systems. Phase equilibrium calculations are also critical for monomer separation or solvent recovery operations.

- Mass transfer: Mass transfer plays a much more important role with polymer systems than with typical chemical systems. For example, addition polymer propagation reaction rate can be controlled by the mass transfer rate of monomers through the highly viscous polymer melt toward polymer reaction sites. Condensation polymer reaction rate can be adversely affected by the condensate concentration that is limited by the transfer rate of condensate from viscous reacting phase to vapor phase. Mass transfer can also be the dominant factor deciding the residual monomer content in stripping operations. Polymer models should take into account the mass transfer phenomena in catalyst modeling, reactor modeling, unit operation modeling, etc.

- Parameter estimation: Rapid and reliable parameter estimation for polymer reaction kinetics is essential for the successful development of an accurate model that covers a wide range of operating conditions. Lack of independent data that would allow the fitting of individual reaction kinetic constants and high level modeling experience significantly increases the necessary time for model development and validation. The use of non-linear multivariable regression techniques integrated with open kinetics equation-oriented models could significantly reduce the required effort by minimizing the number of required experimental or plant data and improving the speed and accuracy of the calculation.

- Structure-property relationship: Polymer producers and their customers define polymer product quality in terms of specific end-use properties rather than polymer molecular structure. For example, polyolefin producers are concerned about Melt Index (MI) or Melt Flow Ratio (MFR). Polyester producers are concerned about color and intrinsic viscosity (IV). Adhesives producers are concerned about peel and shear. Polymer process simulators deliver value to industry only if they correctly compute and track polymer product quality and properties as process conditions change. Therefore, it is essential that polymer modelers find ways to relate end-use properties to polymer molecular structure.

Many of these issues related to polymer modeling have been successfully addressed with innovations in process modeling technologies. Examples include the segment concept in process simulators (Ko et al., 1992), the segment-based polymer activity coefficient model (Chen, 1993), the component attributes concept to quantify polymer molecular structure in process simulators (Barrera et al., 1997), the polymer equation-of-state that builds on segment-based parameters (Gross and Sadowski, 2001), the molecular weight distribution calculation algorithm for linear addition polymers (Hamielec et al., 2000), the flash algorithm for polymer fractionation with molecular weight distribution (Behme et al., 1999; Cheluget et al., 2001), etc.

Industrial Applications

Through advances in polymer process modeling technology and pioneering efforts of industrial champions (Mock et al., 1988; Jackson et al., 1990; Ko et al., 1990; Ramanathan et al., 1992), polymer process modeling has shown its value and its industrial applications expanded quickly. Today it is well accepted in many sectors of polymer industry and numerous successful modeling efforts with significant financial returns have been reported.

Table 1 shows some of the success stories reported by the industry. In general, process modeling is well practiced for condensation polymers such as polyesters, polyamides, polycarbonates, etc. Process modeling is also quite well practiced for major addition polymers such as polystyrene (PS), polyvinyl chloride (PVC), styrene-acrylnitrile copolymer (SAN), low density polyethylene (LDPE), high density polyethylene (HDPE), linear low density polyethylene (LLDPE), polypropylene (PP), EPDM, etc. Emulsion polymerization processes often employ highly complex polymerization chemistry. Applications of polymer process modeling tools for emulsion polymerization (i.e., polyacrylates) and ionic polymerization are less practiced and more experiences are needed. These are emerging areas for polymer modeling and we expect to see more successful industry applications to appear in coming years.

Table 1. Some Industrial Modeling Efforts for Polymer Processes

Polymers	Polymerization Chemistry	Industrial Applications
PBT	Condensation polymerization	Mock et al. (1988); Jackson et al. (1990)
PET	Condensation polymerization	Tremblay et al. (1995); Kang et al. (1997); Tremblay (1999)
Nylon 6	Condensation polymerization	Loth et al. (1998)
Silicone	Condensation polymerization	Mathias et al. (2000)
LDPE	Free radical polymerization	Ko et al. (1990); Orbey et al. (1998); Bokis et al. (2001), Schmidt and Mähling (2001)
HDPE	Ziegler-Natta polymerization	Sirohi and Ramanathan (1998); Cheluget et al. (2001)
PP	Ziegler-Natta polymerization	Schmidt and Mähling (2001)
PS	Free radical polymerization	Loth et al. (1998)
PS	Ionic polymerization	Hungenberg et al. (2001)
Polyacrylates	Emulsion polymerization	Bettenwort et al. (1997)
SBR	Ionic polymerization	Sirohi and Ravindranath (1999)

Polymer process models are now routinely used offline to help develop new processes, design new plants, trouble-shoot existing plants, and optimize plant operations. In addition, polymer process models are increasingly used online to serve as online monitoring systems and to improve on existing control systems (Froisy et al., 1999; Schmidt and Mähling, 2001). This is due to the advancements in integrated process modeling systems and on-line state estimation technology for large-scale first principle models (Papastratos et al., 1999). It is now straight forward to build and validate a steady state polymer process model, to convert the steady state model to a dynamic one that incorporates all controllers, to bring the steady state model online as online calculators for process monitoring purposes, to bring the dynamic model online and have the model state variables validated with real time data, to apply the dynamic model on line as look-ahead predictors, to apply the dynamic model as operator training simulators, etc. The online validated dynamic model can then be used to generate linear state-space models to be used with model predictive controllers. In summary, the investment in developing polymer process models now yields returns in many different ways.

Unsolved Problems and Future Opportunities

Due to the complex nature of polymer chemistry and physics, there are still many unsolved modeling issues and opportunities for future innovations. A few of them are discussed here.

Polymer Thermodynamics

Recent progress in polymer thermodynamic models (including both equations-of-sate and activity coefficient models) has made it possible to develop meaningful polymer process models. However, continuing advances in polymer catalyst development, experimental measurements, and process modeling technology will create new requirements for polymer thermodynamic models. These new requirements may include accounting for complex polymer molecular characteristics such as mixed polymers and polymer microstructures (i.e., block copolymers or alternating copolymers), polymer crystallinity, polymer branching frequency, and copolymer composition distribution. For example, bivariate distributions (such as molecular weight – chemical composition distribution) are becoming more prevalent. Advanced polymer thermodynamic models and polymer flash algorithms that could differentiate the variations in these complex polymer molecular characteristics will be needed.

Transport Properties

Models for transport properties such as thermal conductivity and viscosity play key roles in modeling heat transfer, mass transfer, and sizing process equipments. Currently available transport property models are mainly developed for small molecule systems and their utility for polymer solutions remains very limited. Furthermore, existing transport property models often fail to give the desired accuracy for multi-component mixtures, not to mention the requirement of computing transport properties for polymer slurry solutions. This is a real and daily problem in the industrial practice of polymer process modeling and process development and design. Polymer process modeling could benefit very much from advances in engineering models for transport properties and databanks of validated model parameters for pure component and mixture properties.

Structure-Property Relationship

There is a strong industrial need in polymer process and product design to predict polymer end use properties, such as melt index, based on polymer molecular structure information. However, there is little theoretical basis to relate end-use properties (mechanical or optical or others) to polymer molecular structure. Neural net-based empirical models have not been widely accepted together with first principles process modeling because they do not transform information into understanding and they cannot be used for extrapolation. However, neural net-based models may provide an interim bridge for the missing link in developing models for polymer structure-property relationship.

Mass Transfer

Due to the high viscosity of polymer solutions, mass transfer modeling has been a particularly important component of polymer process modeling. In contrast, mass transfer is often ignored in traditional chemical process modeling. Consequently, existing chemical process simulators do not provide modeling framework or methodology to systematically address mass transfer. When necessary, mass transfer modeling is often introduced as a special case and treated with customized models or user code. A systematic modeling methodology to treat mass transfer as a component of process modeling, in parallel to that of phase equilibrium modeling, will be a major advance in process modeling technology.

Polymer Equipment Models

Polymer manufacturers use many specialized equipments. Examples include fluidized bed reactors, disk-ring reactors, hopper reactors, crystallizers, spray dryers, cyclones, extruders, etc. There can be multiple layers of different granularity in model representations for these equipments. Depending on the needs of process models, equipment models with appropriate level of granularity or fidelity need to be developed and then integrated into process models. When developing these equipment models, modelers should construct these models from modeling components that represent fundamental chemical engineering science and engineering, i.e., reaction engineering, applied thermodynamics, fluid flows, mass transfer, etc.

Polymer Process Models

Developing and validating a polymer process model requires extensive data and modeling expertise in polymer thermodynamics, polymer reaction engineering, and equipment modeling. In order to lower the barrier to develop polymer process models, proven process models for major industrial polymer processes are highly valuable and sought after. These proven process models can be used as a model template and starting point for developing models for specific plants. Limited validation efforts are required to fine tune proven process models for specific plants and the models can quickly become available for use by plant managers or process engineers for various applications. Proven process models are now available for a number of polymer processes. More of them should be developed and the use of non-linear multivariable regression techniques integrated with open-kinetics equation oriented models should reduce the required effort.

Computational Chemistry

While experimental data are rather limited for polymer thermodynamics, transport properties, and reaction engineering, in the future, computational chemistry (or molecular modeling) may help bridge the gap between process modeling requirements and the lack of experimental data. To date, computational chemistry can supply, for small molecules, quantitative estimates of engineering parameters such as heats of formation and heats of reaction, entropies and heat capacities, reaction rate constants, and transport properties like viscosity and thermal conductivity that are needed to construct macro-scale models of complete chemical processes. More recently, efforts by chemical engineers have also advanced techniques for the prediction of phase equilibrium. Due to economic nature and the challenges in dealing with “large-scale” polymer properties, industrial polymer simulations with computational chemistry are much less frequent (Müller-Plathe, 2001). However, we can expect that new computational chemistry techniques or models will evolve and some of them will make significant impact on industrial polymer research, including polymer process modeling.

Computational Fluid Dynamics

Equipment designers and process engineers are increasingly using Computational Fluid Dynamics (CFD) to analyze the detailed flow and mixing processes within individual items of process equipments. CFD allows for an in-depth analysis of the fluid mechanics and local effects in these types of equipments. For example, CFD helps improve understanding on the coupling between micro-mixing and complex polymerization chemistry (Kolhapure and Fox, 2001). For example, CFD may help resolve the prediction of mass-transfer rates by providing a fundamental method to calculate film thickness and surface renewal rates based on physics instead of correlations. In many cases, use of CFD has resulted in improved performance, better reliability, more confident scale-up, improved product consistency, and higher plant productivity. As the CFD techniques advance rapidly, we need to explore ways to couple CFD and process modeling. For example, can we use results of CFD to parameterize the idealized flow reactor models such as continuous-stirred tank reactor or plug flow reactors? Recently, Wells and Ray (2001) suggested a method that unifies CFD simulations and traditional idealized flow reactor models, allowing the detailed information obtained using CFD to be used in computationally simple reactor models. We need more advances like this

Conclusions

For decades chemical engineers have advanced and applied process modeling technology to capture the fundamental engineering understanding of industrial processes and process modeling technology has proven to be a key enabling technology for many successful process design and development efforts in the process industries. The development and application of process modeling technology for the polymer industry is relatively recent. There are unique modeling challenges associated with polymer process modeling, and innovative technologies have been successfully developed to address some of these challenges. The polymer industry has enthusiastically embraced process modeling technology and generated proven business benefits. While the practice of polymer process modeling is being widely accepted, polymer process modeling technology is still in its early stage of development. Future innovations are needed to address many unsolved challenges and new opportunities resulting from complex polymer chemistry and physics.

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