

Dynamic Modeling of Modified Styrene-Acrylonitrile Process

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Abstract: Dynamic model for the commercial modified styrene-acrylonitrile (SAN) polymerization process is developed using the custom modeler within Aspen Dynamics (R). Modified SAN is one of the most widely used thermoplastics in commercial products. In the commercial modified SAN process, the polymerization reaction takes place under high temperature. However, most of the studies of modified SAN process in the past have been conducted under low temperature. Thus, it is difficult to predict the properties, such as weight-average molecular weight, number-average molecular weight, and polydispersity index, of polymer with the models studied in the past. We develop a dynamic simulation model considering segment-based approach, group contribution method, and first principles such as thermodynamic equations and reaction kinetics. Polymer properties are calculated from method of moments, and the model is validated by comparing the properties of simulation result with measured data from plant experiments. Our model gives better performances than the models developed in the past, which are built under different process conditions from the process of interest.

Keywords: Modified SAN, Dynamic modeling, Process simulation, Polymerization kinetics, Aspen Plus,

1. INTRODUCTION

Acrylonitrile butadiene styrene (ABS) resin is a thermoplastic polymer that is widely used as interior, exterior material of automobiles, home appliances, and IT devices, for it has stable mechanical properties. One of the ABS resin types is poly(styrene-acrylonitrile), so-called SAN, produced by copolymerizing styrene(SM) and acrylonitrile(AN). SAN is an industrially preferred material due to its good chemical resistance, transparency, rigidity, and processability. In order to add high heat resistance to its characteristics, α -methylstyrene (AMS) is introduced as a third monomer to generate poly(α -methylstyrene-styrene-acrylonitrile) terpolymer, which is called modified SAN.

Building a model of modified SAN process is important because modified SAN is a product of high economic value. A robust model describing phase equilibrium, polymerization kinetics, physical, and thermodynamical properties can be applied to design, control, and optimize polymerization process, helping to reduce cost and increase benefit. Up to now, some models have been proposed to simulate the modified SAN process. Garcia-Rubio et al. (1985) developed a mathematical model of bulk SAN polymerization. The model includes global mass balance, free volume theory, and autoacceleration of the reaction rates from gel effect to consider diffusion-controlled environment condition. Experimental data are made at low temperatures be-

low 60°C in glass ampoules, and are compared with model predictions. A mathematical model for describing modified SAN suspension polymerization reactors was proposed by Cavalcanti and Pinto (1997). Assuming free radical kinetic mechanism, kinetic parameters were collected from open literature. Global mass balance, momentum balance, energy balance, thermodynamic equilibrium equations were considered. The differential algebraic equations from the balance and equilibrium equations were solved by computer code DDASSL. Another approach was suggested by Sharma (2000). Different compositions and temperatures of monomers were polymerized, followed by measuring the weight average molecular weight, MW_W , and number average molecular weight, MW_N . Then, an empirical relation between MW_W , monomer concentration, and weight fractions of each monomer was obtained from regression, without considering the complex reaction kinetics.

However, models developed in the past are not applicable universally. The past models were constructed under different operating conditions from the target process, such as reactor types, reactor arrangements, temperature range of reactions, and monomer compositions. If the past models are applied to the target process as they are, accurate predictions of polymer properties including MW_N , MW_W , and polydispersity index (PDI), the ratio of MW_W to MW_N cannot be guaranteed due to extrapolation. Hence, a different model is required for each process condition.

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In this work, we develop a dynamic model for the commercial modified SAN polymerization process using Aspen Dynamics (R), applying conditions consistent with our process of interest. The objective of this work is to build a digital twin that represents similar behavior of the polymerization process of interest, considering its process conditions and suggesting new kinetic mechanisms with new kinetic parameters. The rest of the paper is organized as follows. Section 2 describes the process of interest. Section 3 provides the methodologies used in this work. Section 4 explains the procedure of the modified SAN process modeling. Section 5 gives the result of simulations, and compares it with the experimentally measured molecular weights and PDI of modified SAN. Finally, Section 6 provides concluding remarks.

2. PROCESS DESCRIPTION

The process of interest, which is from a proprietary industrial plant, is depicted in Fig. 1. Two CSTRs are arranged in series, respectively connected with a tank that captures vapor phase. The vapor phase comes from the liquid phase monomers and solvent due to polymerization heat and high reaction temperature. Next, the vapor phase reactants are condensed into liquid phase in the tanks, and are recovered to each reactor. Devolatilizer for monomer recovery and pelletizer follow the second reactor. Polymer products from pelletizer are then transported into silos, except a small amount of polymer samples collected to measure MW_W , MW_N , and PDI via laboratory analysis. It is noteworthy that SM, AN, AMS, and initiator are mixed with the monomers and solvent recycled from devolatilizer, and then are divided into three to be injected to the first reactor and each tank. By doing so, the concentration of monomers are kept relatively high in the reactors. The process is free radical bulk polymerization, achieves monomer conversions of about 40 and 65 percent in the first and second reactor, respectively. Reactor temperature ranges from 100°C to 120°C, and reactor pressure does not exceed 3 bar. Reactor temperature, reactor pressure, reactor level of liquid phase reactants, monomer flow rates, and initiator flow rate are known to be key variables for the control of process.

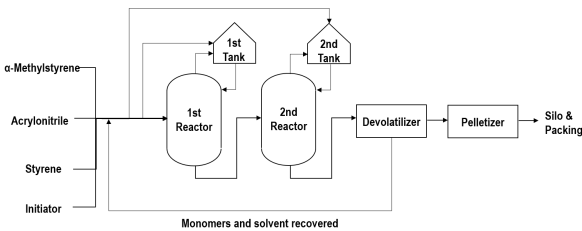


Fig. 1. Schematic diagram of modified SAN polymerization process

3. METHODOLOGIES

3.1 Segment-based approach

The segment-based approach considers a polymer chain is made up of a series of segments (Heil and Prausnitz,

1966; Skjold-Jørgensen, 1984; Hu et al., 1991). Segment-based approach can express the non-ideality of a solvent-polymer mixture by connecting it with newly introduced solvent-segment binary interaction parameters. Segment acts as a repeat unit (-R), and has a well defined molecular structure. Each segment corresponds to each monomer used to grow polymer molecule.

3.2 Group contribution method

Thermodynamic properties of materials are estimated by group contribution method if specific property values are not present. Properties are calculated depending on the types and numbers of functional groups of the molecular structure. Van Krevelen group contribution method is a method for predicting segment property parameters of heat capacity, molar volume, enthalpy, entropy, glass transition temperature, and melt transition temperature (Van Krevelen, 1990). UNIFAC (UNIQUAC functional group activity coefficients) is a method for predicting non-electrolyte activity in non-ideal mixtures (Fredenslund et al., 1975). UNIFAC estimates binary interaction parameters of Polymer-NRTL activity coefficient model, which will be discussed in Section 3.3 (Fredenslund, 2012).

3.3 Polymer-NRTL activity coefficient model

Polymer-NRTL activity coefficient model is developed to explain the phase behavior of a polymer system which is different from general chemical systems. Physical and thermodynamic properties of a polymer molecule are distinguished from general molecules because a polymer molecule consists of a large number of repeated segments. Therefore, special thermodynamic models are needed to take the difference into account (Bokis et al., 1999). Polymer-NRTL activity coefficient model is an extended version of the NRTL (Non-random two-liquid) model (Renon and Prausnitz, 1968), and is known for its good performance in showing the physical and thermodynamic properties of polymer systems (Chen, 1993; Renon and Prausnitz, 1968; Seavey et al., 2003; Zhang et al., 2002).

In the Polymer-NRTL model equations, the Gibbs free energy of mixing a polymer solution is the sum of the enthalpy of mixing, which is calculated based on NRTL theory and the entropy of mixing, which is calculated based on the Flory-Huggins theory (Flory, 1941; Huggins, 1941) to consider the molecular size difference between polymers and small molecules. The relationship is expressed as in (1).

$$\begin{aligned} \frac{\Delta G_{mixing}}{RT} &= \frac{\Delta H_{mixing}^{NRTL}}{RT} - \frac{\Delta S_{mixing}^{FH}}{R} \\ &= \sum_s n_s \frac{\sum_j x_j G_{js} \tau_{js}}{\sum_j x_j G_{js}} + \sum_p n_p \sum_i r_{i,p} \frac{\sum_j x_j G_{ji} \tau_{ji}}{\sum_j x_j G_{ji}} \\ &\quad + \sum_I n_I \ln \phi_I \quad (1) \end{aligned}$$

Also, activity coefficient of each component species, γ_i , is multiplied by the activity coefficient of interactions term from NRTL theory and the size (entropic) term from Flory-Huggins theory :

$$\ln \gamma_I = \ln \gamma_I^{FH} + \ln \gamma_I^{NRTL} \quad (2)$$

where

$$\ln \gamma_I^{FH} = \ln \left(\frac{\phi_I}{x_I} \right) + 1 - m_I \sum_J \left(\frac{\phi_J}{m_J} \right) \quad (3)$$

$$\ln \gamma_{I=p}^{NRTL} = \sum_i r_{i,p} \left[\frac{\sum_j x_j G_{ji} \tau_{ji}}{\sum_k x_k G_{ki}} + \sum_j \frac{x_j G_{ij}}{\sum_k x_k G_{kj}} \left(\tau_{ij} - \frac{\sum_k x_k G_{kj} \tau_{kj}}{\sum_k x_k G_{kj}} \right) \right] \quad (4)$$

$$\ln \gamma_{I=s}^{NRTL} = \frac{\sum_j x_j G_{js} \tau_{js}}{\sum_k x_k G_{ks}} + \sum_j \frac{x_j G_{js}}{\sum_k x_k G_{kj}} \left(\tau_{sj} - \frac{\sum_k x_k G_{ks} \tau_{ks}}{\sum_k x_k G_{kj}} \right) \quad (5)$$

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij}) \quad (6)$$

$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T} + e_{ij} \ln T + f_{ij} T \quad (7)$$

$$\alpha_{ij} = c_{ij} + d_{ij}(T - 273.15) \quad (8)$$

The Polymer-NRTL model requires binary interaction parameters and nonrandomness factors of solvent-solvent, solvent-segment, segment-segment. The binary parameters, τ_{ij} , and nonrandomness factors, α_{ij} , are independent of molecular weight, concentration, and composition of polymer molecules, but depends on temperature as shown in (7) and (8). α_{ij} is normally set to 0.3 for its weak temperature dependency (Prausnitz et al., 1998). Positive value of τ_{ij} indicates repulsion (e.g. interaction between hydrophobic and hydrophilic species) and negative value of τ_{ij} indicates attraction (e.g. interaction between two hydrophilic species) (Chen and Song, 2004).

3.4 Method of moments

Polymer products have a distribution in molecular weights, because a polymer solution is composed of polymer molecules with different chain length. To avoid calculating the full distribution of polymer molecular weight every second in a dynamic simulation, method of moments is introduced to calculate average polymer molecular weight (Bamford and Tompa, 1953; Biesenberger and Sebastian, 1983). k_{th} moment of chain length distribution, λ_k , is defined as

$$\lambda_k = \sum_{n=1}^{\infty} n^k [D_n] \quad (9)$$

Polymer properties and equations to calculate the polymer properties using method of moments are listed in Table 1. From the equations in Table 1, the zeroth moment of chain length distribution, λ_0 , means the total flow rate of chain length distribution, λ_1 , means the total flow rate of polymer segments. Degrees of polymerization, molecular weights, and PDI are calculated from the ratios of zeroth, first, and second moment of chain length distribution.

Table 1. Polymer properties calculated using method of moments

Property	Description	Equation
λ_0	Zeroth moment of chain length distribution	$\lambda_0 = \sum_{n=1}^{\infty} n^0 [P_n]$
λ_1	First moment of chain length distribution	$\lambda_1 = \sum_i \lambda_1(i)$
$\lambda_1(i)$	Mole flow of segments of type i	$\lambda_1(i) = \sum_{n=1}^{\infty} n^1 [P_n(i)]$
λ_2	Second moment of chain length distribution	$\lambda_2 = \sum_{n=1}^{\infty} n^2 [P_n]$
$F_p(i)$	Mole fraction of segments of type i	$F_p(i) = \lambda_1(i) / \lambda_1$
$\overline{M_{seg}}$	Average segment molecular weight	$\overline{M_{seg}} = \sum_i F_p(i) M(i)$
DP_N	Number-average degree of polymerization	$DP_N = \lambda_1 / \lambda_0$
DP_W	Weight-average degree of polymerization	$DP_W = \lambda_2 / \lambda_1$
MW_N	Number-average molecular weight	$MW_N = DP_N \overline{M_{seg}}$
MW_W	Weight-average molecular weight	$MW_W = DP_W \overline{M_{seg}}$
PDI	Polydispersity index, which determines the broadness of polymer chain molecular weight distribution	$PDI = DP_W / DP_N$
LCB	Number of long chain branches	Calculated from kinetics
$FLCB$	Long chain branching frequency	$FLCB = 10^3 LCB / \lambda_1$

4. PROCESS MODELING

In this paper, a dynamic simulation model of the process in Section 2 is developed for polymer property prediction. The process conditions at which our model is simulated are identical with the conditions the actual plant was operated. Its performance is compared with the model developed by Cavalcanti and Pinto (1997), and with the measured polymer properties from actual plant data. It is important to emphasize that the model developed by Cavalcanti and Pinto (1997) collected reaction mechanisms and kinetic parameters from the open literature, at temperature conditions under 60°C. The validation of the model by Cavalcanti and Pinto (1997) was also carried out under the low temperature conditions of the model.

4.1 Reaction kinetics

There are some free radical polymerization reaction mechanisms suggested in literature (Brandrup et al., 1999; Cavalcanti and Pinto, 1997). However, long chain branch of polymer molecule, which is considered to be an important characteristic of polymer, is not taken into account if following the existing reaction mechanisms. For the model to consider long chain branch, the reaction mechanisms (16), (17), and (19) which were not suggested in the past studies of modified SAN are suggested in this work. Total reaction mechanisms are as follows:

$i, j : SM, AN, AMS$

Chain initiation

· *Initiator decomposition*



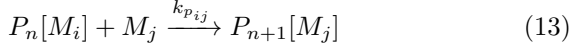
· *Styrene thermal initiation*



· Primary chain initiation

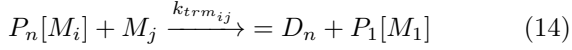


Propagation

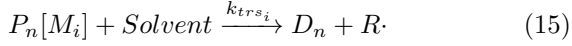


Chain transfer

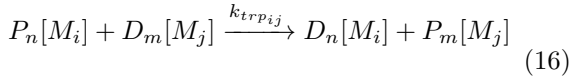
· To monomer



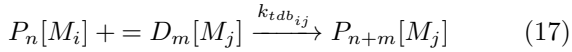
· To solvent



· To polymer

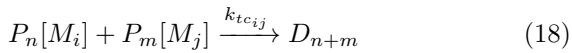


Terminal double bond polymerization

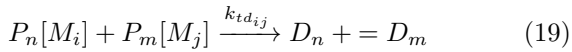


Termination

· By combination



· By disproportionation



4.2 Kinetic parameter adjustment

The reaction rate constants were expressed by the Arrhenius equation as follows:

$$k = k_{ref} \exp\left[\frac{-(E_a + \Delta VP)}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right] \quad (20)$$

Kinetic parameters including pre-exponential factor, k_{ref} , activation energy, E_a , activation volume, ΔV , and reference temperature, T_{ref} were determined for each reaction rate constants. Owing to the low pressure condition of the process of interest, all values of ΔV were assumed to be zero. Initiator efficiency, ϵ , was assumed to be 0.5. Kinetic parameters of reactions except (16), (17), and (19) are suggested in the literature (Hui and Hamielec, 1972; Brandrup et al., 1999; Tsoukas et al., 1982; Rudin and Chiang, 1974), yet the simulation results did not match the polymer properties measured in actual plant when using the literature value of parameters.

To match the polymer properties with actual plant data, the k_{ref} values of (12) and (13), were adjusted from the open literature by multiplying 1.9, and (18) by multiplying 0.5. The E_a and T_{ref} were not adjusted to reduce the number of parameters changed. The k_{ref} and E_a values of (16), (17), and (19) are not available in literature, and the k_{ref} values of (16) and (17) were adjusted by multiplying 0.02 to the k_{ref} values of (14). The k_{ref} values of (19) were adjusted by multiplying 0.5 by the literature k_{ref} values in (18). E_a and T_{ref} values of (16) and (17) were set to the same value of (14), and E_a and T_{ref} values of (19) are identical with the E_a and T_{ref} values of (18).

4.3 Dynamic simulation modeling

For dynamic simulation modeling, segment-based approach was applied as shown in Fig. 2. SM-R, the segment of SM, corresponds to SM. AN-R and AMS-R correspond to AN and AMS in the same way. Thermodynamic properties of segments were calculated by van Krevelen group contribution method. The vapor-liquid equilibrium of polymer system is calculated using Polymer-NRTL activity coefficient model and Redlich-Kwong-Soave (RKS) cubic equation of state (Redlich and Kwong, 1949; Soave, 1972). Binary interaction parameters in (7) were estimated from UNIFAC. Polymer properties such as MW_N , MW_W , and PDI were calculated by method of moments. Then, the polymer properties over time were calculated when time-series process data including reactor temperature, reactor pressure, reactor level of liquid phase, monomer flow rates, and initiator flow rate were incorporated into the dynamic simulation model.

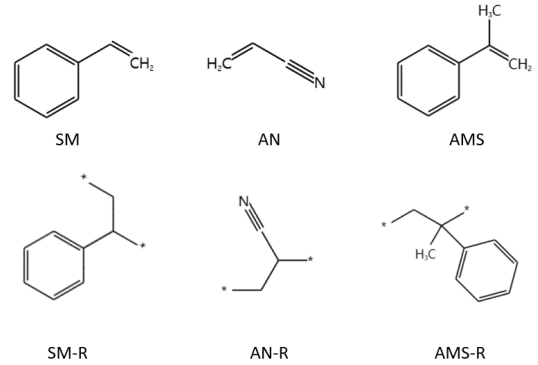


Fig. 2. SM, AN, AMS and their corresponding segments

5. SIMULATION RESULTS AND DISCUSSION

The simulated process time is 1974 hours. Process conditions such as inlet reactant and inert gas flow rates, reactor temperature, reactor pressure, and liquid level of reactors and tanks are the input of the model. For the comparison of the performance of our new model, dynamic model based on Cavalcanti and Pinto (1997) was applied to the modified SAN polymerization process and simulated with the identical process conditions of our new model. The past model does not consider the reaction mechanisms (16), (17), and (19), and kinetic parameter adjustment. MW_W , MW_N , and PDI values of our new model and the past model were compared with the measured data from actual plant described in Section 2. Our new model and past model were evaluated with the root mean square error (RMSE) and the mean absolute percentage error (MAPE) to the measured data. The RMSE and the MAPE are defined as:

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^n (y_i - \hat{y}_i)^2} \quad (21)$$

$$MAPE = \frac{100}{n} \sum_{i=1}^n \left| \frac{y_i - \hat{y}_i}{y_i} \right| \quad (22)$$

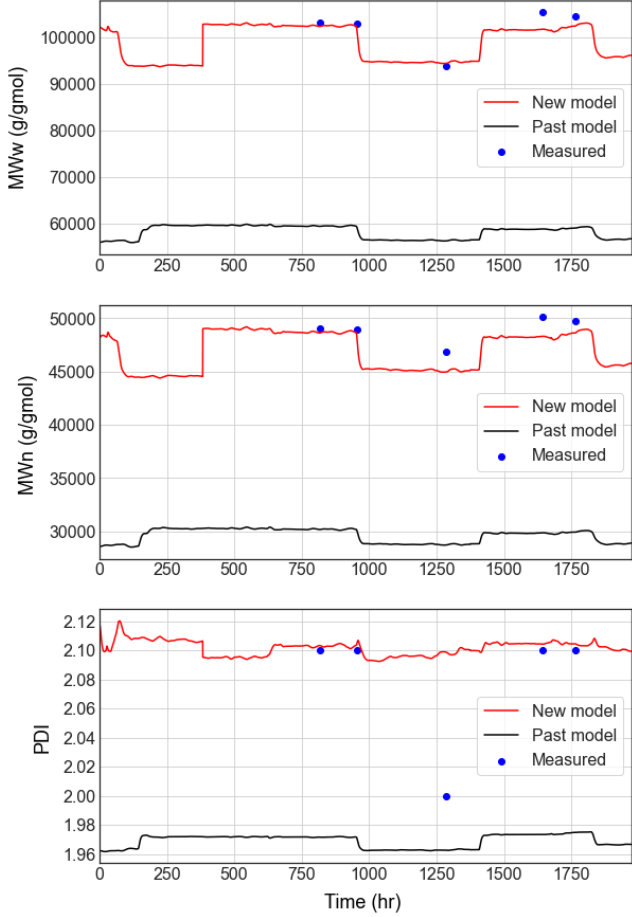


Fig. 3. MW_W , MW_N , and PDI dynamic simulation results of the new model and the past model

where n is the number of measurement points, y_i and \hat{y}_i are the measured and predicted value of MW_W , MW_N , and PDI, respectively. The results of dynamic simulation is shown in Fig. 3, and the performance evaluation of models is summarized in Table. 2

As shown in Fig. 3 and Table. 2, the new model shows better performance than the past model. In the new model, MW_W , MW_N , and PDI values are higher than the past model. MW_W , MW_N values can be explained by comparing λ_0 , λ_1 , and λ_2 values of our new model with the past model in Fig. 4. From Table. 1, the value of MW_W is proportional to λ_2 and inversely proportional to λ_1 . λ_1 and λ_2 values of our new model increase because the k_{ref} values of (12) and (13) are increased as described in Section 4.2. Increased k_{ref} values in (12) and (13) lead to increased λ_1 , the total flow rate of segments in polymer molecules. λ_2 increases more rapidly than λ_1 from (9), resulting in the increase of MW_W . Similarly, the value of MW_N is proportional to λ_1 and inversely proportional to λ_0 . Unlike λ_0 and λ_1 , λ_0 value decreases in our new model because k_{ref} values in (12) and (13) increase with the sum of the k_{ref} values in (18) and (19) conserved. The decrease in λ_0 and increase in λ_1 result in the increase in MW_N . The increase in PDI value can be explained by considering (16), (17), and (19). Reactions affecting long chain branch are known to increase the PDI value (Shroff and Mavridis, 1995).

Table 2. Evaluation results of the new model and the past model

	New model		Past model	
	RMSE	MAPE	RMSE	MAPE
MW_W	2100.63	1.73	43390.37	42.42
MW_N	1360.57	2.55	19236.5	39.248
PDI	0.044	1.1486	0.115	5.2279

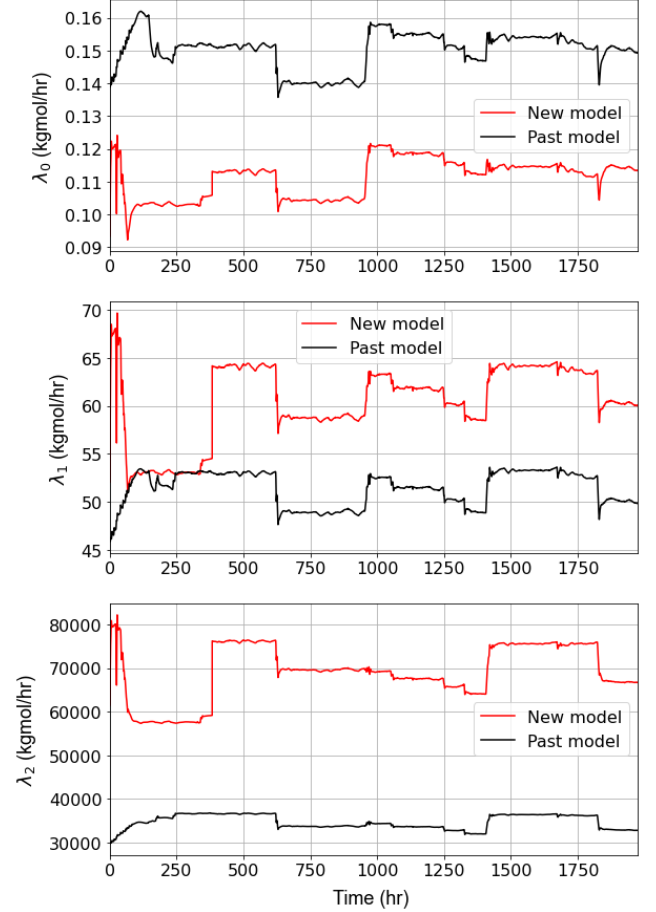


Fig. 4. λ_0 , λ_1 , and λ_2 dynamic simulation results of the new model and the past model

6. CONCLUSION

In this work, we suggest a dynamic model for an industrial modified SAN polymerization process and compare its prediction performance with the past model and measurement data. Reaction kinetics were modified from literature to consider the long chain branch which was ignored in the past studies. Some kinetic parameters were adjusted from literature, while the other kinetic parameters were newly suggested to match polymer properties with the measurement data of the target process in high temperature and low pressure condition. With the ability to predict more accurate values of polymer properties by considering long chain branch reactions and kinetic parameter adjustment, our model outperforms the past models.

For further research, parameter estimation techniques can be applied to improve the prediction performance of our model, tuning the kinetic parameters determined by trial and error in this work.

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