

Development of a Dynamic Model for the Production of Impact Modified Styrene/Maleic Anhydride Copolymers

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Presentation Outline

- Model purpose and objectives
- Model development
 - Thermodynamic and thermo-physical properties
 - Kinetic scheme
- Model results
- Conclusions

Model Purpose and Objectives

- Predict reactor performance during unsteady state operating conditions
- Optimize reactor steady state operating conditions
- Optimize grade transitions strategies to minimize off-grade products
- A training tool off-line for engineers and technicians at the plant site

Model Purpose and Objectives (cont.)

- Use of the model will help reduce risks especially going to plant trials (i.e. to ease scale-up of new commercial product formulations) by:
 - Targeting conditions
 - Predicting overall performance
- Predict Polymer properties
- Test various system configurations, such as dual reactors versus a single CSTR

Selection of a Property Method for the Thermodynamic Properties

- A property method is a collection of methods and models that Aspen Properties uses to compute thermodynamic (fugacity coefficients, enthalpy, entropy, Gibbs free energy, and volume) and transport (viscosity, thermal conductivity, diffusion coefficients, and surface tension) properties.

Selection of a Property Method for the Thermodynamic Properties (cont.)

- Ideal Property Methods (Ideal gas/Raoul' s Law/Henry' s Law)
- Equation Of State (EOS) Property Methods (SAFT– Statistical Associating Fluid Theory, Sanchez–Lacombe, ect...)
- Activity Coefficient Property Method (Flory–Huggins, Polymer NRTL–Non–Random–Two–Liquid model)

Selection of a Property Method for the Thermodynamic Properties (cont.)

- Activity Coefficient Property Method is selected
 - Versatile , accommodate a high degree of solution none-ideality into the model
 - Can only be used for the liquid phase, another model is needed for the vapor phase (usually an equation of state)
- Polymer Non-Random Two-Liquid (Poly-NRTL) model is used for the calculation of the activity coefficients of the system and the related physical properties.

Selection of a Property Method for the Thermodynamic Properties (cont.)

- Poly-NRTL is a segment-base model that allows accurate representation of copolymer composition and chain length
- The Van Krevelen Thermo-Physical property models are used to calculate segment property parameters (such as heat capacity, molar volume, enthalpy, entropy, Gibbs energy of formation, glass transition and melt transition temperatures), which are in turn used to calculate polymer property parameters.

The SMA Model

- Model based on fundamental polymerization principles with a full Free-Radical polymerization kinetic scheme for the system Styrene, MA, and Rubber
- Aspen Plus was used to generate the properties file
- Aspen Dynamics and Aspen Custom Modeler were used for the dynamic simulation

The SMA Model (cont.)

- Model developed and validated for 2 peroxides
- Input to the model includes: Feed composition, reactor operating conditions, rubber mix composition and degree of polymerization
- Output from model includes: Polymer production rate, polymer composition, M_n , and M_w

The SMA Kinetic Scheme (Free-Radical Polymerization)

➤ Peroxide Decomposition



The SMA Kinetic Scheme (cont.)

➤ Chain Initiation

- $R^* + \text{STY} \rightarrow P_1[\text{STY-SEG}], R_{in1} = K_{in1} C_{\text{STY}} R^*$
- $R^* + \text{MA} \rightarrow P_1[\text{MA-SEG}], R_{in2} = K_{in2} C_{\text{MA}} R^*$

➤ Thermal Initiation

- Free radicals can also be generated from styrene monomer by thermal mechanism. The thermal initiation mechanism for styrene is believed to be 3rd order in monomer. The rate of thermal initiation (R_{th}) is given by:

- $R_{th} = K_{th} C_{sty}^3$

The SMA Kinetic Scheme (cont.)

➤ Chain Propagation



$$\rightarrow R_{p11} = k_{p11} C_{\text{STY}} P_n[\text{STY-SEG}]$$



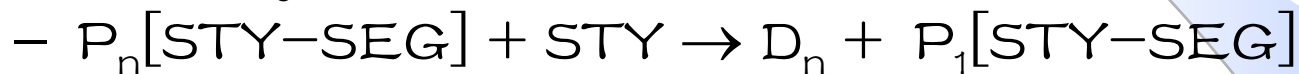
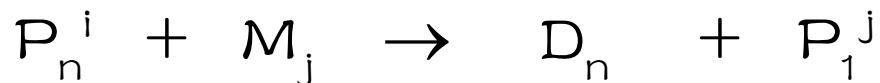
$$\rightarrow R_{p12} = k_{p12} C_{\text{MA}} P_n[\text{STY-SEG}]$$



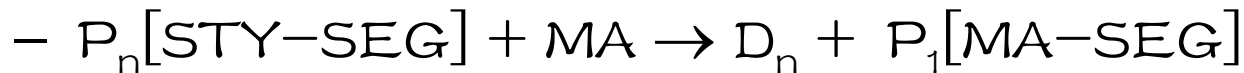
$$\rightarrow R_{p21} = k_{p21} C_{\text{STY}} P_n[\text{MA-SEG}]$$

The SMA Kinetic Scheme (cont.)

➤ Chain Transfer to Monomer

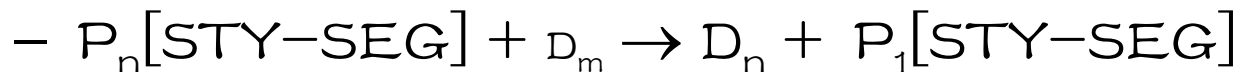
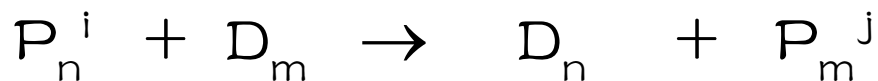


$$\rightarrow R_{tm11} = K_{tm11} C_{\text{STY}} P_n[\text{STY-SEG}]$$



$$\rightarrow R_{tm12} = K_{tm12} C_{\text{MMA}} P_n[\text{STY-SEG}]$$

➤ Chain Transfer to Polymer



$$\rightarrow R_{tp11} = K_{tp11} C_{\text{STY}} P_p[\text{STY-SEG}]$$

The SMA Kinetic Scheme (cont.)

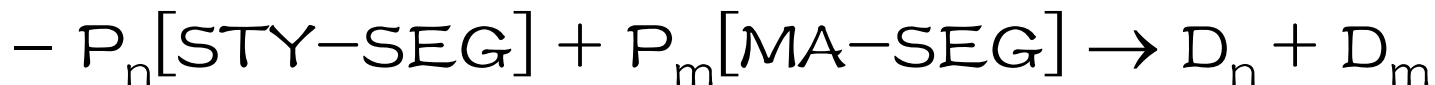
➤ Terminations reactions



$$\rightarrow R_{tc11} = K_{tc11} P_n[\text{STY-SEG}] P_m[\text{STY-SEG}]$$



(disproportionation)



$$\rightarrow R_{tp12/21} = K_{tp21/12} P_n[\text{STY-SEG}] P_m[\text{MA-SEG}]$$

Gel Effect

- The gel effect (Trommsdorf effect) is modeled by multiplying the termination reaction rate coefficients, K_o , by a Gel Factor (GF).
- GF decreases with increasing conversion (GF vary between 0 and 1).
- The effective rate coefficient (K_{eff}) for the Termination reaction is given by:

$$K_{eff} = K_o GF$$

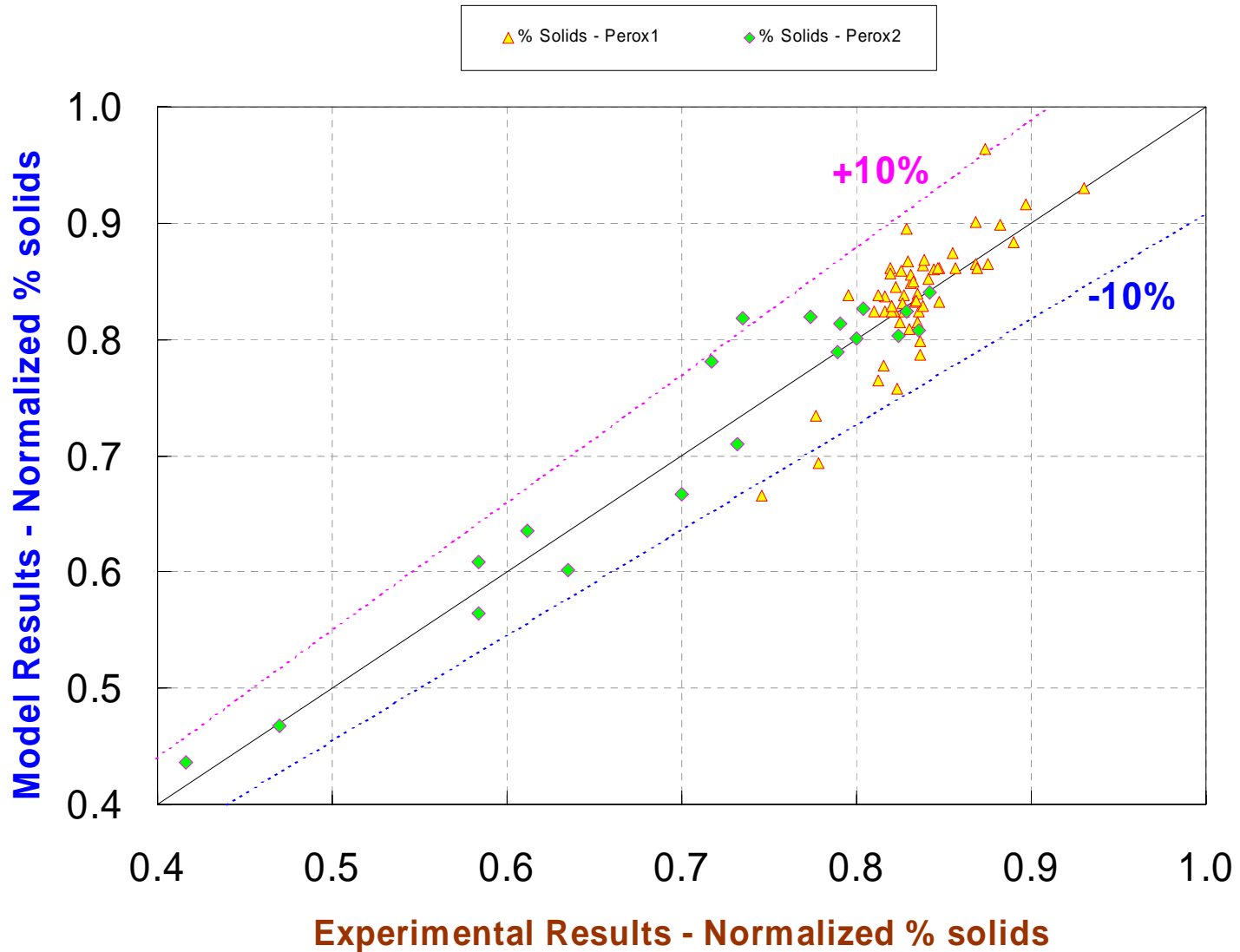
Gel Effect (cont.)

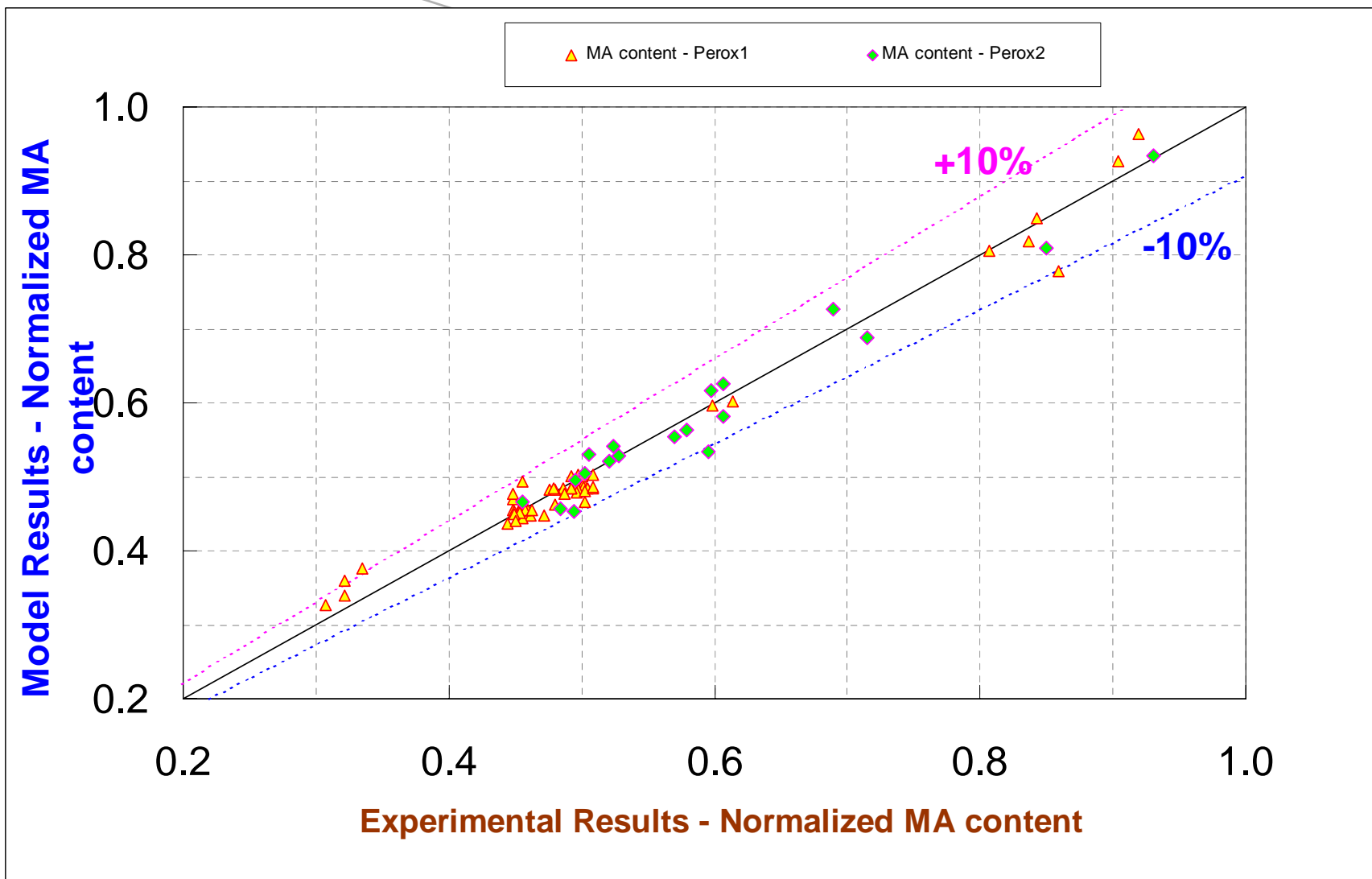
- GF correlation selected is a function of reactor conversion only
- $GF = a_1 / (1 + a_2 X_p^{a_3})$

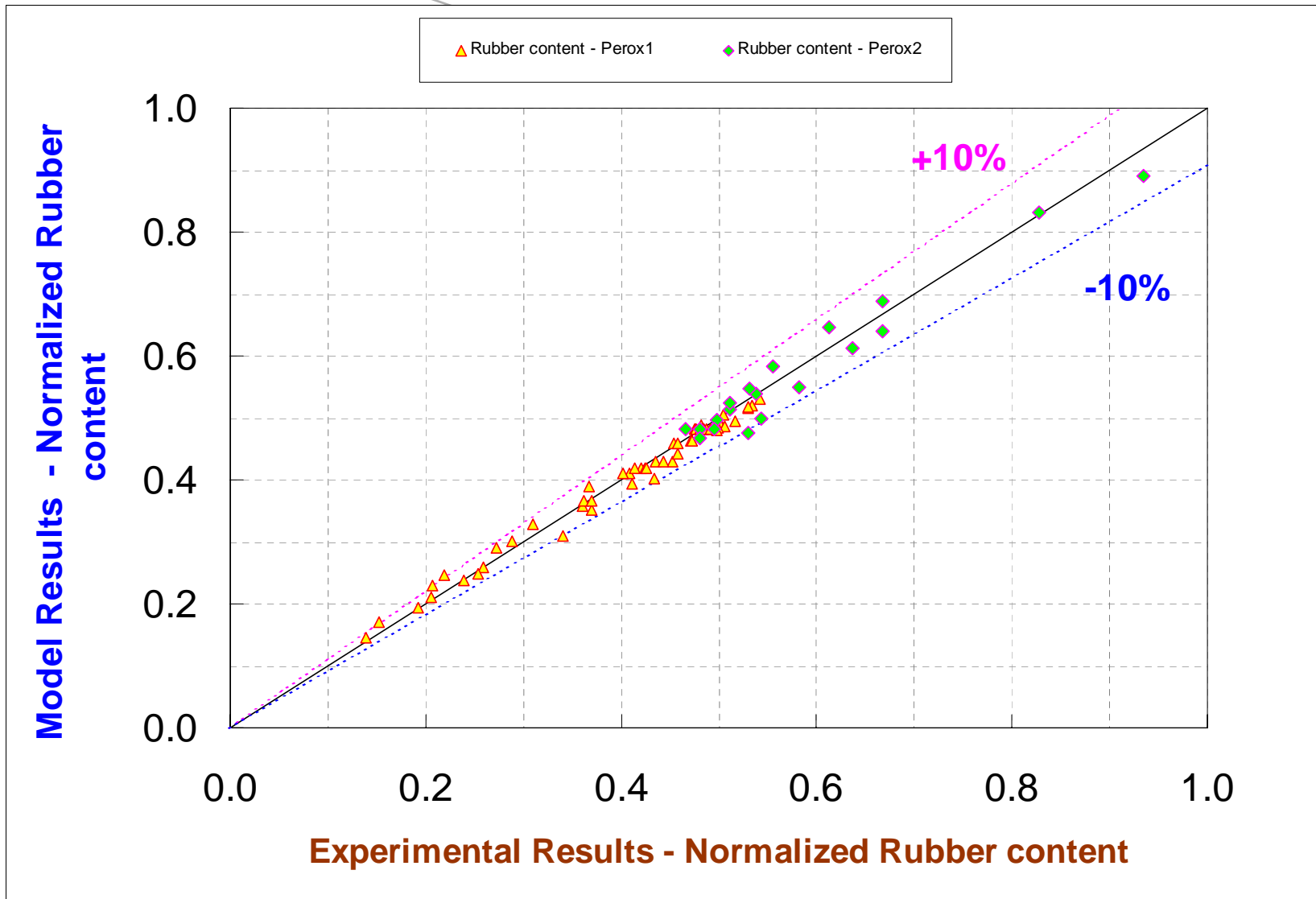
Where

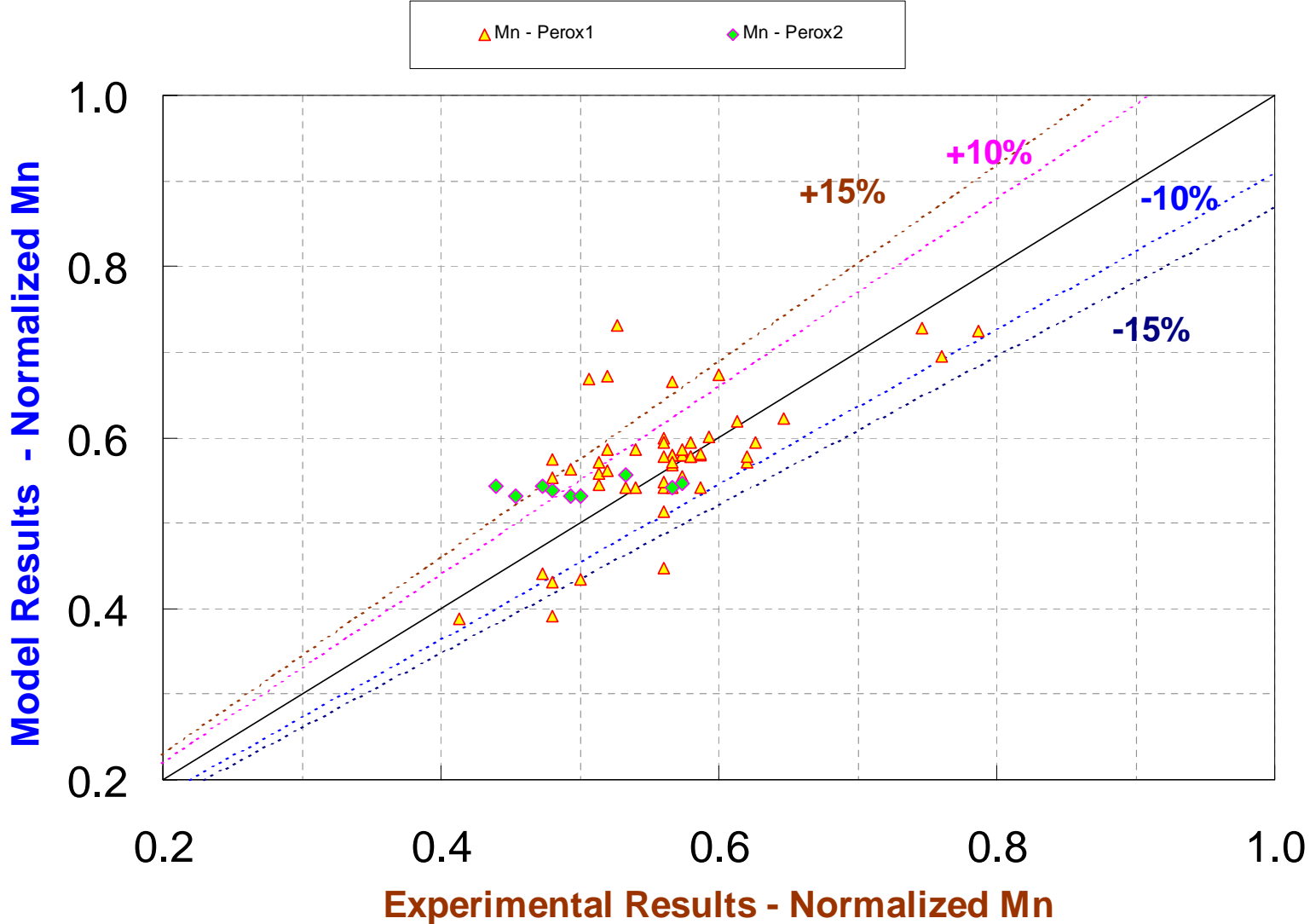
X_p = weight fraction of the polymer

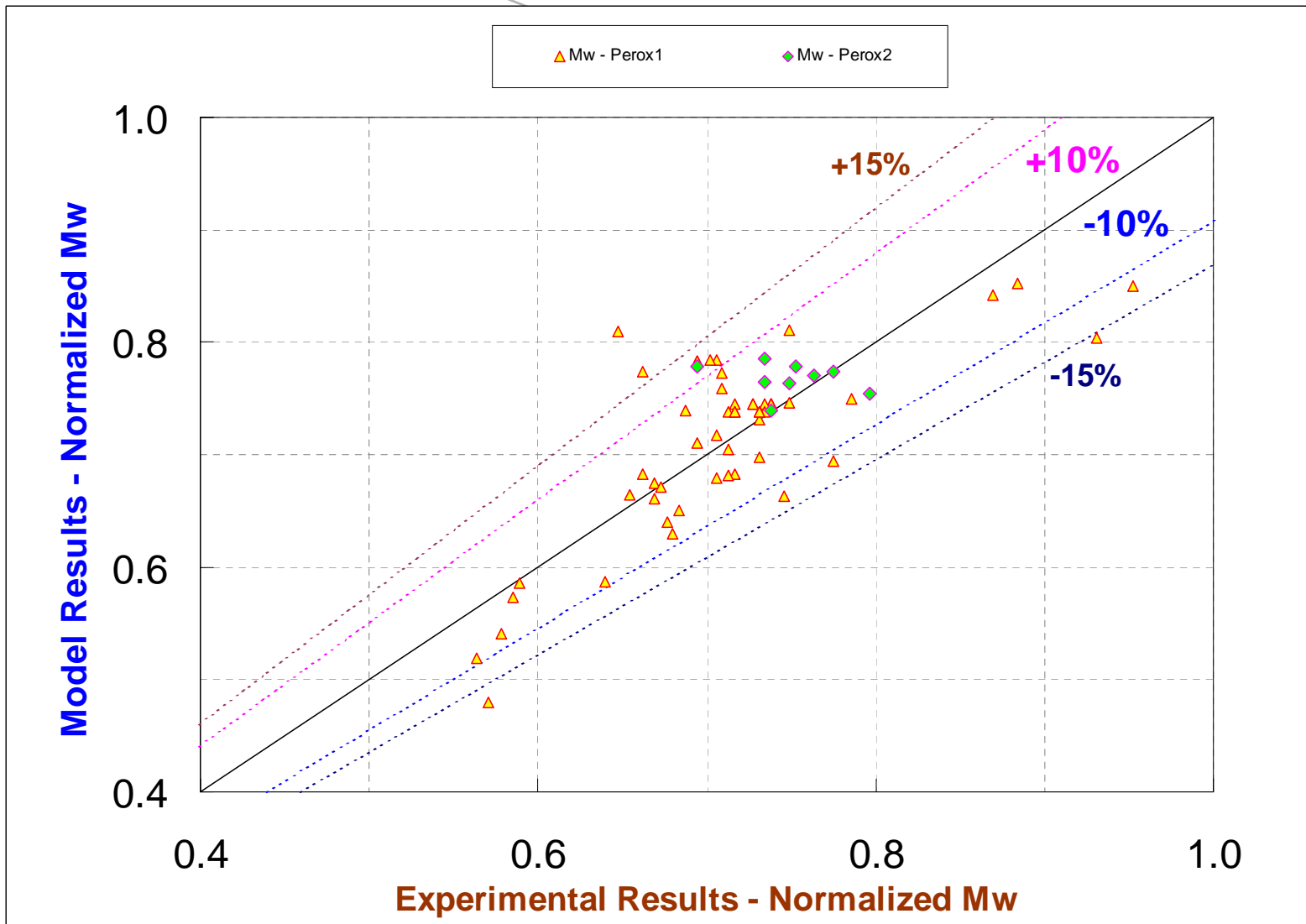
a_1 , a_2 and a_3 are user specified parameters

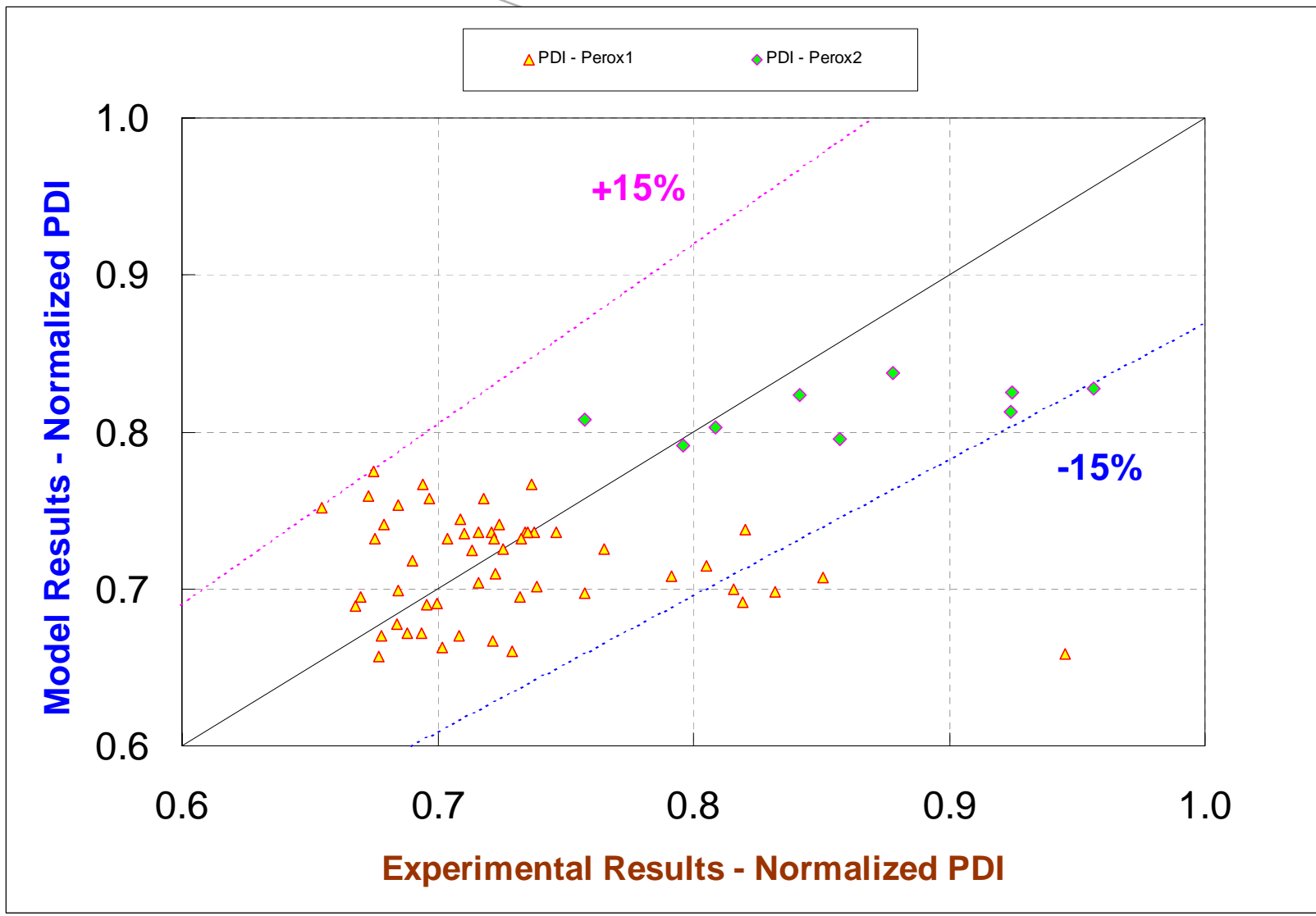












Conclusions

- A dynamic model was successfully developed and used to estimate the kinetic constants for the free-radical polymerization scheme for the system styrene/MA/rubber.
- Model predictions for the percentage solids and the polymer compositions were within $\pm 10\%$ compared to the experimental data.
- For M_n , model predictions in 73% of the cases were within $\pm 10\%$ of the experimental data and in 85% of the cases were within $\pm 15\%$ of the experimental data.

Conclusions (Cont.)

- For M_w , model predictions in 82% of the cases were within $\pm 10\%$ of the experimental data and in 93% of the cases were within $\pm 15\%$ of the experimental data.
- PDI predictions in 92% of the cases were within $\pm 15\%$ of the experimental data. These results are in line with the experimental data considering the accuracy of the experimental measurements of M_n and M_w .

Conclusions (Cont.)

- The model was successfully validated using experimental runs that were not originally used for the estimation of the kinetic parameters.
- The present dynamic model constitute a versatile tool for process optimization and developments of new polymer recipes.

Acknowledgements

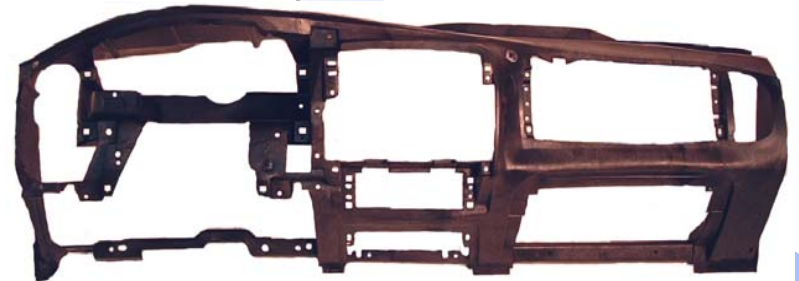
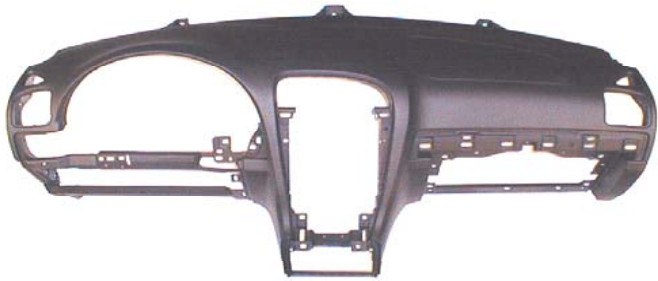
- Beaver Valley analytical lab for the polymer composition analysis and the polymer molecular weights

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