Industrial EP(D)M Rubber Production Process: a First-Principle Data-Driven Modelling Approach

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Ethylene-Propylene-(Diene) rubber is one of the most worldwide used polymers, employed in a large variety of applications. Versalis EP(D)M is produced by suspension copolymerization, without the use of solvent, initiated by metallorganic component (Ziegler-Natta catalysts).
In this work, a first-principle model to evaluate the performance of an industrial EP(D)M plant production is proposed. The polymerization mechanism was implemented in an Aspen Polymers v12.1 simulation of the industrial plant. Model parameters were tuned based on process data for selected product grades; model performance was cross-validated with further product grades and production line data. By leveraging external code (e.g., MATLAB/Python), process engineers can automate the tuning procedure, and accelerate sensitivity/optimization analysis. Both steady-state and dynamic simulations can successfully be employed to improve process understanding, analyse past conditions, monitor plant performance, and explore future process/product developments.

1. Introduction

Ethylene-propylene elastomers are synthetic rubbers that are prepared by polymerization of ethylene, propylene, and optionally a non-conjugated diene. They are random, amorphous polymers with outstanding resistance to ozone, ageing, weather, and high temperatures due mainly to their saturated backbone structure. Main applications for ethylene-propylene elastomers include automotive parts, single-ply roofing, appliance parts, modification of other polymers (thermoplastic olefins), wire and cable, hoses, and viscosity index improvers for lubricating oils. Two types of ethylene-propylene elastomers are currently produced: (i) Ethylene-Propylene Copolymers, which contain a saturated chain and require vulcanization by means of free radical generators such as organic peroxides or a combination of peroxides and sulphur, and (ii) Ethylene-Propylene Terpolymers, which are essentially ethylene-propylene-diene terpolymers that have a saturated chain and a diene in the side chain.

The first Versalis EP(D)M production plant via suspension technology (60 kt/y) is on stream since 1974 at Versalis site in Ferrara (Italy); in 1991 a new line was built increasing the plant capacity up to 100 kt/y, and in 2018 a further line with a capacity of 48 kt/y was started-up. Two more lines, with an overall capacity of 96 kt/y, are on stream since 2017 in the Far East (Versalis, 2022). In the following sections, EP(D)M polymerization and industrial plant are briefly introduced.

1.1 EP(D)M polymerization

EP(D)M elastomers are produced by polymerizing ethylene and propylene with a small amount (3-12%w) of a nonconjugated diene; the most used diene in the manufacture of EP(D)M is ethylidene norbornene (ENB) (NexantEAC, 2022). There are two primary systems used to produce EP(D)M: Ziegler-Natta and Metallocene catalyst (NexantEAC, 2022; Baldwin and Ver Strate, 1972). Ziegler-Natta catalysts consist of a transition metal salt and an organometallic compound, also known as a co-catalyst. The interaction between these compounds, through a multi-step process, leads to the formation of the active site for reactions. The mechanistic aspects of
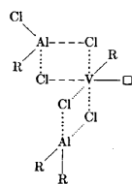
Figure 1: Possible structure of a complex containing both vanadium and aluminium.

the polymerization have been studied mainly with titanium catalyst because precursors components are easily isolated and identified; only a few vanadium based systems are fully understood (Ver Strate, 1986). Vanadium-aluminum alkyl halide combinations produce complexes soluble in nonpolar hydrocarbon; a possible structure of a complex containing both vanadium and aluminum is shown in Figure 1. A variety of such structures can be drawn, and in many cases more than one structure appears to exist, as the product polymer is a superposition of individual component polymers; the presence of multiple species affects the molecular weight distribution (MWD) and the compositional distribution of the polymer.

The active oxidation state of vanadium is +3, with reduction from +4 or +5 occurring upon alkylation. An inactive oxidation state of +2 can be reactivated by treatment with promoters that may increase catalyst efficiency.

A Ziegler-Natta catalyst polymerizes olefins by inserting them into the metal-carbon bond. The mechanism starts with the reaction between the transition metal compound and an aluminum alkyl, or similar, to give a metal-carbon bond and a coordinative unsaturation (activation of the catalytic site). Then, the monomer approaches the catalytic site and coordinates with the metal. Finally, the monomer inserts in the metal-carbon bond (chain migratory insertion). After the insertion, a new coordinative unsaturation on the metal is formed and the chain reaction can proceed. Features such as the number and type of ligands of the transition metal, their steric hindrance, and the ionic nature of the bond have dramatic importance on the insertion reaction and hence on the copolymer characteristics.

There are numerous Ziegler-Natta combinations, each of which offers varying levels of performance. The patent and scientific literature describes methods of synthesizing catalysts with improved characteristics such as higher activity and improved control of molecular weight (Baldwin and Ver Strate, 1972; Ver Strate, 1986).

After years of internal development, Versalis has introduced an improved new Ziegler-Natta catalyst system based on vanadium. The new catalyst system was scaled-up to the industrial plant and used in a slurry process to obtain new EP(D)M grades (Perretta and Vallieri, 2013; Di Pasquale, 2017).

Manufacturers utilize the flexibility of the catalyst performance to produce grades with a variety of characteristics (variety of molecular weights, range of ENB, ethylene and propylene percentages) for special applications.

1.2 EP(D)M industrial plant

Ethylene and a mixture of propylene and propane are fed to the polymerization reactor (see Figure 2) together with pre-catalyst, co-catalyst and activator (and ENB in case of EP(D)M production). Hydrogen is added as a molecular weight controller. Since the reaction is exothermic and temperature and pressure have to be kept constant in the reactor, a direct thermostatic system based on compression and recycle of reaction vapours is provided. Rubber crumbs are formed in the reactor and float in a liquid monomer phase.
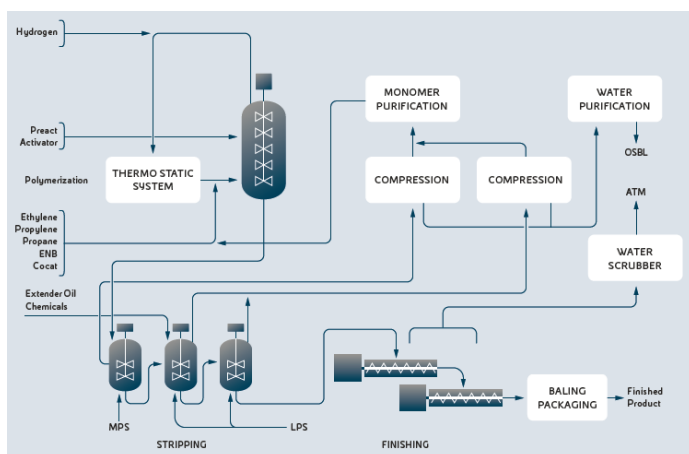

Figure 2: EP(D)M industrial plant process scheme.

Ethylene conversion is about 99%, while propylene conversion is around 30% and depends on production rate and type. Reaction behaviour is controlled by a proprietary advanced control system and a gas chromatograph analysers on the reactor vapour phase for continuous control of the concentration of the monomers. The polymer slurry discharged from the reactor is sent to a high pressure stripper in presence of water, with small amounts of stripping additives and antioxidants. Medium pressure steam is injected to remove part of the unreacted monomers, recycled water from finishing is charged to the stripper to keep constant the watery slurry ("crumb slurry") concentration. The crumb slurry is pumped to the low-pressure stripper, where most of the residual monomers is removed from the crumbs by low pressure steam injection. The slurry is then transferred to the next low-pressure stripper, where the remaining monomers are stripped by low pressure steam. The crumb slurry is then fed to the finishing section.

Steam and monomer vapours leaving the high- and low-pressure strippers pass through a filter and then are condensed by an air-cooler and cooling water heat exchangers; the gas phase (mainly propylene and propane) is compressed and sent to the monomers distillation section. The liquid phase, composed of water and ENB, is recovered and sent to storage for further purification. Monomers recovered from the stripping section are distilled in order to remove light and heavy impurities before being recycled into the reactor. The purified monomer is separated from the reflux stream, refrigerated, and sent through a coalescer to the alumina columns package in order to reduce water content before being stored in a buried tank. This tank is refilled with propylene and propane to control the composition fed to the polymerization. From the storage tank the monomers are sent to the polymerization section through a molecular sieve columns package to drop down water and polar components. Monomer stream is continuously analysed with an on-line gas-chromatograph. In Finishing Section, rubber crumbs pass through a primary shaker screen and two extruders (dewatering press and mechanical dryer) in order to remove the water and obtain the final dry product. The polymer almost completely dewatered is sent to the final drying section where hot air is injected to keep warm the product and reduce the content of water up to the final specification value. The product discharged from the top of the vertical spiral conveyor drops into the baling package, bales are then wrapped with a film of polyethylene in the bales wrapping machine and are sent to the packaging. In the finishing area, fumes, with a small quantity of VOC, coming out from equipment are sent to a water scrubber before being discharged into the atmosphere. Water and fines coming from the primary shaker screen and dewatering press are collected to the recycle fines tank, a stirred tank from which water and fines are recycled to the stripping section. Excess water is removed from the recycle fines tank by overflow and discharged to the finishing sump.

2. Model

In this section, the model implemented in the Aspen simulation is described, along with its calibration strategy and cross-validation.

2.1 First-Principle model description

The developed model refers to the reaction section, i.e. the reactor itself with inlet and outlet streams, along with the thermostatic system; stripping and finishing sections, as well as recovery, purification and ancillary sections are not included in the model.

From the thermodynamics perspective, the approach chosen in the simulation was the "POLYSRK" (Aspen Technology Inc., 2021), which is a special version of the "Predictive-SRK" adapted for simulations that include polymerization reactions. "Predictive-SRK" (Holderbaum and Gmehling, 1991) consists of a modified version of the Soave-Redlich-Kwong cubic equation of state, proposed by Soave (1972).

From the kinetics perspective, the polymerization scheme used in the simulation accounted for the phases of (i) catalyst activation, (ii) polymer chain initialization, (iii) polymer chain propagation, and (iv) polymer chain termination.

During the catalyst activation phase (Figure 3), pre-catalyst and co-catalyst interaction eventually leads to the
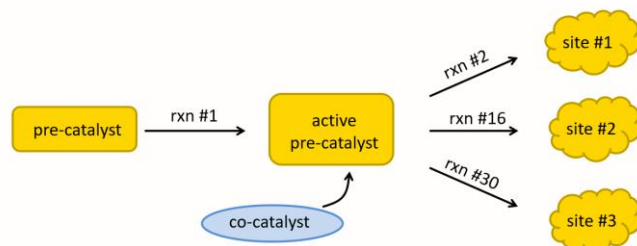

Figure 3: Pre-catalyst activation, complexation by co-catalyst, and active sites formation.
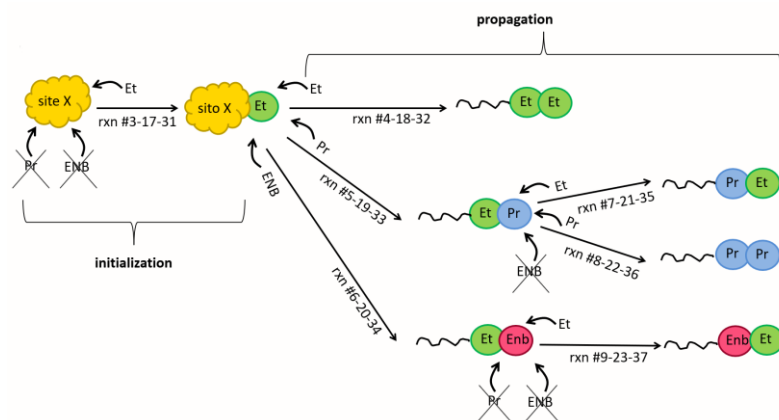
Figure 4: Polymer chain initialization and propagation.

formation of a plurality of active sites, which may differ for their reactivity to the monomers and to the polymer chain. A detailed implementation of this reaction phase may be cumbersome and may lack the necessary experimental data for the required calibration; thus, in this work a simplified approach was used: first the pre-catalyst is transformed into its active form, and then n. 3 reactions describe the interaction of the active pre-catalyst with the co-catalyst which leads to the formation of n. 3 active sites. The kinetic constants involved in these 3 reactions can be tuned to address the desired active site distribution.

Once the catalyst has turned on (i.e., active sites are formed), the polymerization chain may start with the initialization phase (Figure 4). In this work, only chain initialization via ethylene was considered, while propylene and ENB initialization were discarded. Each active site has its own ethylene initialization kinetics.

After the first ethylene monomer reacts with the active site, polymer chain propagation may occur: ethylene, propylene or ENB can propagate the chain when ethylene is the last monomer in the chain; ethylene or propylene can propagate the chain when propylene is the last monomer in chain; only ethylene can propagate the chain when ENB is the last monomer in the chain. Each active site has its own propagation kinetics. Other possible propagations were discarded.

Two mechanisms were considered for polymer chain termination (Figure 5): a spontaneous (thermal) chain termination, and hydrogen chain termination. After termination, the reaction site is no longer active, but may be turned on again by the activator. In this work, site reactivation by the activator was not detailed, and thus the site is promptly active and available after polymer chain termination, i.e. the termination acts like a chain transfer agent. Each active site has its own termination kinetics.

Pre-catalyst activation, active site formation, and polymer chain initialization were considered temperature independent; polymer chain propagation and termination were considered temperature dependent in an Arrhenius-like form, i.e. pre-exponential factor and activation energy were introduced.

From the process simulation perspective, the reactor can be approximated by an ideal Continuous-flow Stirred-Tank Reactor (CSTR); the thermostatic system may be omitted (i.e., implicit thermostatic system) and its effect included in the heat duty removed from the reactor, or it can be explicitly detailed considering an adiabatic reactor. The explicit approach is more precise and allows sensitivity analysis on the operative conditions of the thermostatic system; on the other hand, it is much more computationally expensive and less stable due to the recycle stream. Thus, the implicit approach may be convenient for the initial calibration of the model.
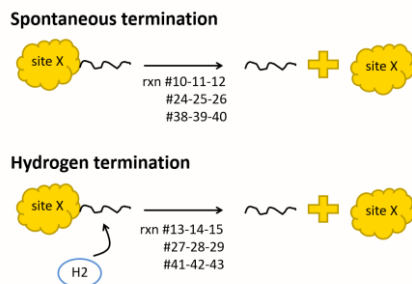

Figure 5: Polymer chain termination.

2.2 Data-driven model calibration and cross-validation

The kinetic model described in §2.1 is made of #43 reactions: #7 reactions are temperature independent, #36 reactions are temperature dependent. Some simplifications and assumptions may apply, e.g. constant proportionality or identity, leading to further parameter reduction. Exhaustive plant data used for calibration and cross-validation are confidential information of Versalis, therefore cannot be disclosed here; a synthetic and normalized form of the data used for model calibration and cross-validation are reported in Table 1 and 2, respectively. Three product grades were employed for model calibration, which differentiate for rubber throughput productivity, polymer chain composition (ethylene, propylene, and ENB where applicable), molecular weight (MWW) and polymer dispersity index (PDI). For model cross-validation, a 4th grade was employed, and data from the same plant and from a smaller production line were collected. For all grades, stable stationary plant data were used, and multiple plant runs at higher/lower rubber productivity levels were employed, which are not reported here.

Table 1: Experimental plant production data used for model calibration (normalized wrt Grade A).

Product grade	Rubber productivity	Ethylene composition	Propylene composition	ENB composition	MWW	PDI
A	1.00	1.000	1.000	1.000	1.00	1.00
B	1.04	1.161	0.658	0.929	0.86	1.33
C	0.88	1.178	0.659	0.000	0.91	1.09

Table 2: Experimental plant production data used for model cross-validation (normalized wrt Grade A).

Product grade	Rubber productivity	Ethylene composition	Propylene composition	ENB composition	MWW	PDI
D	0.94	0.975	1.038	1.476	1.02	1.00
D*	0.91	0.978	1.028	1.484	1.03	1.00

* plant data from a different (smaller) production line.

Tuning the model, i.e. finding the parameter values that minimize the model calibration error, may require running multiple process simulations and may be somewhat cumbersome. By leveraging external code (e.g., MATLAB/Python), this procedure can be automated using a least-squares method. An example of Python code for an Aspen simulation batch run is reported in Figure 5. Optimization can be run using Python SciPy library, e.g. using optimize.minimize function and an appropriate objective function definition.

```python
# library import
import win32com.client as win32

# open Aspen engine
Aspen = win32.gencache.EnsureDispatch('Apwn.Document')

# open Aspen simulation
Aspen.InitFromArchive2('C:\aspen_file_path\aspen_file_name.apw')

# set a simulation input variable value
Aspen.Tree.FindNode('input_variable_call').Value = 123456789
# see aspen Aspen variable explorer for appropriate variable_call

# run the simulation
Aspen.Engine.Run2()

# get a simulation output variable value
myvariable = Aspen.Tree.FindNode('output_variable_call').Value

#close simulation
Aspen.Application.Quit()
```

Figure 5: Python code template for Aspen simulation batch run.

3. Results and discussion

Model parameter values that came from the calibration procedure are confidential information of Versalis, therefore cannot be disclosed here; overall model performance is reported in Table 3. Errors are reported wrt actual plant data, i.e. the error is the ratio between the difference predicted-real value and real value. Grades A, B, and C were used for model tuning, thus these errors represent the calibration error; Grades D and D* were used for cross-validation. Calibration errors are well below 10%, cross-validation errors are larger, as expected, but still acceptable. The largest errors are for Grade D*, i.e. a product grade that was not used for model calibration and with data from a different production line, suggesting that plant instrument accuracy may affect model prediction capability, although it is still considered acceptable.

Table 3: Model performance (error percentage wrt plant data value).
Grades A, B, C: calibration error; Grades D, D: cross-validation error.*

Product grade	Rubber productivity	Ethylene composition	Propylene composition	ENB composition	MWW	PDI
A	+1.12%	-0.22%	+0.56%	-2.34%	+1.97%	+0.93%
B	-2.46%	+0.19%	-0.52%	-3.09%	+0.28%	+0.00%
C	+0.64%	-0.18%	+0.67%	n.a.	-5.68%	-0.85%
D	+1.32%	-0.25%	+0.70%	-3.14%	-9.24%	+0.00%
D*	+3.09%	+2.54%	-4.76%	-6.98%	+13.2%	+0.93%

The proposed model was used by Versalis elastomer process engineers to perform sensitivity analysis for alternative operation conditions, troubleshoot plant upset conditions, and to anticipate and explore possible plant conditions for product grades under development at the lab/pilot scale. Model parameters were transferred to a dynamic simulation, allowing for plant dynamics investigations, e.g. input disturbance step response, plant start-up/shut-down, and plant control improvement.

Although the present model prediction capability is considered acceptable, further improvements in accuracy and robustness may come from calibration dataset expansion to further product grades and different plant run conditions.

4. Conclusions

Versalis EP(D)M slurry technology was introduced, and EP(D)M polymerisation was briefly presented. A first-principle model for an industrial plant reaction section was derived and implemented in an Aspen Polymers simulation environment. Plant data for different grades were used to calibrate the model, using a Python script to automate the procedure. Model accuracy was cross-validated with a further product grade and an alternative production line. Model accuracy was well below 10% for most cases, thus model predictions can be considered accurate and used for sensitivity analysis, plant optimization, and product development.

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