Proprietary process technology

EP(D)M

Ethylene Propylene Diene Monomer terpolymers

Versalis proprietary process technologies available for licensing

Our company

Versalis - the petrochemical subsidiary of Eni - is a dynamic player in its industry sector facing the multifold market needs through different skills.

With a history as European manufacturer with more than 50 years of operating experience, Versalis stands as a complete, reliable and now global supplier in the basic chemicals, intermediates, plastics and elastomers market with a widespread sales network.

Relying on continuous development in its production plants as well as in its products, strengthening the management of the knowledge gained through its long industrial experience, Versalis has become a worldwide licensor of its proprietary technologies and proprietary catalysts. The strong integration between R&D, Technology and Engineering departments, as well as a deep market expertise, are the key strengths for finding answers to customers requirements.

Our commitment to excellence, in quality of our products and services, makes our company an active partner for the growth of customers involved in petrochemical business.

Through engineering services, technical assistance, marketing support and continuous innovation, our knowledge is the key strength to customize any new project throughout all phases.

Customers can rely on this strong service-oriented outlook and benefit from a product portfolio that strikes a perfect balance of processability and mechanical properties, performance and eco-friendliness.

Introduction to Versalis EP(D)M technology

EP(D)M is an Ethylene-Propylene-(Diene) rubber produced by suspension copolymerization, without the use of solvent, initiated by metallorganic component (Ziegler-Natta catalysts). EP(D)M is one of the most worldwide used polymers, employed in a large variety of applications. The unusually wide range of products achievable by the Versalis proprietary technology covers all EP(D)M field of application like appliances, cables, polymer modification, viscosity index improver, automotive, bitumen modification, buildings, mechanical goods and TPV.
A good elastomer is a material able to change and recover the shape when a force is first applied and then removed, these characteristics are supplied by a long and flexible chain proper of polyethylene, but this polymer is crystalline: the copolymerization between Ethylene and alpha olefins as Propylene drops down the melting point and creates an amorphous polymer with elastic properties. EPR are saturated rubber so it would be necessary a peroxide post-modification. In order to have a common sulphur curing, a small quantity of Diene (ENB) is added to promote the presence of not saturated links.

Key features of Versalis EP(D)M production technology are:

- high flexibility in terms of product mix and good quality constancy and reproducibility;
- high efficiency compared with the solution process;
- monomer purification is not so critical as for solution process and this reduces purification costs (not comparable with metallocenic processes);
- no solvent recovery system is necessary and consequently the environmental impact is low;
- catalyst is very effective, thus the monomer purification is not so critical as for solution process (less purification costs);
- process vents composition, rich of hydrocarbons, allows to use them as fuel instead of sending them to flare, thus reducing operating cost;
- great attention to all the environmental issues in design, according to the BAT as well as to the IISRP suggestions to the E.U. Authorities;
- lower dimensions of recovery section leads to lower capital investment;
- rejected monomer quantity can be reduced thanks to a specific section design allowing reduction of slop quantity; Versalis is able to design this recovery section based on both client needs as well as site conditions;
- optimized configuration of the stripping section with three stages arrangement to minimize steam consumption without impact emissions of VOC;
- small quantity of volatile organic compounds enter finishing section (low release during extrusion).

Versalis can always provide appropriate solutions to different client's needs thanks to its capabilities and experience in the following fields:

Research & Development

The presence of a strong R&D team, established in Ravenna and Ferrara since the early 70s, qualifies Versalis as an outstanding owner of know-how in the field of elastomers. Reliable and updated facilities (pilot plants, synthesis and analytical labs, equipment for elastomer processing), allow Versalis to continuously up-to-date the technology in order to support the elastomers business in a very competitive and demanding market scenario. Additional services are then available for potential Licensees, such as technical assistance, training, development of analytical methods, site assistance for start-up and follow up, development of tailor made products on demand.

Process design & operational experience

Process design is flexible and able to face different conditions and constraints. Any project is individually evaluated to offer the best solution, tailored to specific customers needs. Thermal and fluodynamic analysis (CFD) can be applied to the design of key equipment such as reactors, agitators and strippers.

The design takes also advantage of the Versalis long-term manufacturing experience.
New technological solutions are first tested in production plants and the acquired experience transferred to the licensed technology, in order to reach not only the best process performances, but also a safe and reliable plant arrangement.

Mechanical design

Versalis Engineering Dept. has been working in close coordination with the Process Dept. since a long time. This fact has allowed to develop unique and well sound engineering solutions for critical equipment, that guarantee the best results in terms of mechanical reliability and process performances.

Versalis EP(D)M technology allows to provide with a single line a fairly broad range of economically feasible capacities up to 50 kt/y per reaction unit with a single finishing line.

Wastes and emissions

The design of the plant is carried out taking into account the target of the minimization of the effluents, as this means more efficiency and lower environmental impact. The process produces oily waste water which can be treated in a normal bio-treatment. Large waste air emissions from finishing require only a scrubbing process (dedusting). Normal process venting are collected and can be sent to flare or other OSBL systems. Solid waste material, during normal operation, is limited to small amounts of filtering elements, plastic cans used as chemicals' package and rubber cleanings from paved areas.

Industrial applications

Versalis is currently one of the major industrial producer of EP(D)M polymer. The first EP(D)M production plant via suspension technology (60 kt/y), based on two polimerization lines, is on stream since 1974 at the Versalis site in Ferrara (Italy). In 1991 a new line was built growing the plant capacity up to 100 kt/y. Two more lines, with an overall capacity of 96 kt/y, are on stream since 2017 in the Far East. A further line with a capacity of 48 kt/y has been recently (2018) started-up in Ferrara site.

Main process parameters

	per MT of dry EPR
Raw material (Ethylene + Propylene)	1,030 kg
Electricity	1.0 MWh
Steam (medium pressure + low pressure[1])	3.5 MT
Cooling water (ΔT + 8 °C)	370 m^3

[1] 18 barg and 5 barg respectively.

	per MT of dry EP(D)M
Raw material (Ethylene + Propylene + ENB)	1,030 kg
Electricity	1.2 MWh
Steam (medium pressure + low pressure[1])	6.0 MT
Cooling water (ΔT + 8 °C)	370 m^3

[1] 18 barg and 5 barg respectively.

	per MT of oil extended EP(D)M
Raw material (Ethylene + Propylene + ENB + oil extensor)	1,040 kg
Electricity	1.0 MWh
Steam (medium pressure + low pressure[1])	4.5 MT
Cooling water (ΔT + 8 °C)	370 m^3

[1] 18 barg and 5 barg respectively.

The Dutral® EP(D)M copolymers and terpolymers portfolio

EP(D)M rubber are available in a range of molecular weight and Mw distribution, ethylene and propylene content.

All these rubber characteristics affect rubber properties:

- increasing Ethylene content, tenacity and thermoplastic behaviour will increase;
- increasing Propylene content, low temperature performances will increase;
- increasing Mw, loading capacity and profile shape stability will increase, while permanent deformation will decrease;
- decreasing Mw/Mn, extrusion and injection performances and cross linking efficiency will increase.

The unusually wide range of products achievable by the Versalis proprietary technology covers all EP(D)M field of application like appliances, cables, polymer modification, viscosity index improver, automotive, bitumen modification, buildings, mechanical goods and TPV. Such portfolio of products is continuously improved by our R&D centers through market feedback.

EP(D)M rubber general properties:

- excellent resistance to ageing, weathering and ozone;
- good resistance to both high and low temperature, from -55 to 150 °C;
- excellent dielectric properties;
- good resistance to organic and inorganic acids, alkalis, polar solvent;
- low permanent set values;
- extremely extendable (filler/oil).

Process description

Ethylene and a mixture of propylene and propane are fed to polymerization reactor together with Pre-Catalyst, Co-Catalyst and activator (and ENB in case of EP(D)M production). Hydrogen is added as molecular weight controller.

Since the reaction is exothermic and temperature and pressure must be kept constant in the reactor, a direct thermostatic system based on compression and recycled of reaction vapours is provided. Rubber crumbs are formed in the reactor and float in a liquid monomer phase. Ethylene conversion is about 99% while propylene conversion is around 30% and depends on production rate and type. The reaction's behaviour is controlled by a proprietary advanced control system and a gas chromatograph analyzers on the reactor vapour phase for a continuous control of the concentration of the monomers.

The polymer slurry discharged from reactor is sent to an high pressure stripper in presence of water with small amounts of stripping additives and antioxidant. 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 the majority 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 is 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 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 by water and ENB, is recovered and sent to a storage for a further purification.

Monomers recovered from stripping section have to be distilled in order to remove light and heavy impurities before being recycled into 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 in order to control the composition fed to the polymerization. From the storage tank the monomer are sent to the polymerization section through a molecular sieve columns package in order to drop down water and polar components.
Monomer stream is continuously analysed with an on-line gas-chromatograph.
In Finishing, 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.

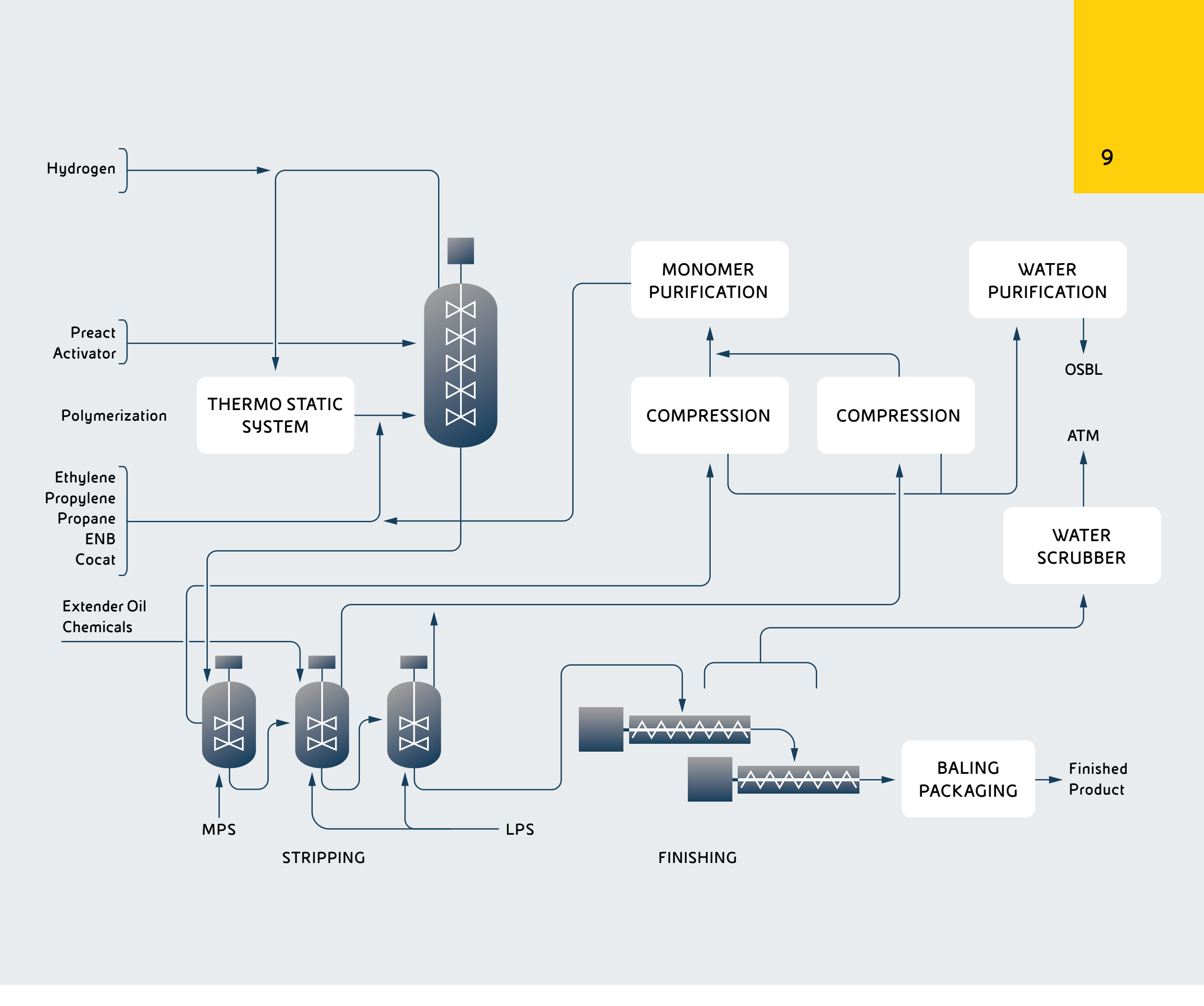
The product discharged from the top of the vertical spiral conveyor drops into the baling package, bales are then wrapped with a film of polyethylene in the bales wrapping machine and are sent to the packaging. In the finishing area, fumes, with small quantity of VOC, coming out from equipment are sent to a water scrubber before being discharged to 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 is discharged to the finishing sump.

Process design advanced features

- Proprietary design of reactor and thermostatic system that allows high efficiency in polymerization related to high solid content (around 15-25%) and high capacity to cool down the system with a reliable and effective temperature control.
- Wide range of product grades, coupled with a real process know-how that enables to meet the specific needs of each customer even for niche productions.
- Process vents composition, rich of hydrocarbons, allows to use them as fuel instead of sending them to flare, with an equivalent capacity of up to 1 t of low pressure steam per t of rubber.
- Water recycle: all the watery phases are recovered and recycled to the process; only the steam fed to the stripping section is discharged from the finishing line and is sent to OSBL (the VOC content is negligible).
- Water pre-treatment: water streams to be sent to biological WWT are pre-treated ISBL with a dedicated section.
- VOC captation: gaseous process streams from plant areas are collected to be connected to flare or other OSBL systems, also during maintenance operations.
- Additives and chemicals: additives and chemicals supplying and handling has been deeply studied in order to minimize cycle openings.
- Rejected monomer quantity can be reduced thanks to a specific section design allowing reduction of slop quantity. Versalis is able to design this recovery section based on both client needs as well as site conditions.

fig. 1

EP(D)M • process scheme



Proprietary process technologies portfolio

Biotech

PROESA® 2G Ethanol and Cellulosic Sugars

Phenol and derivatives

Cumene (with PBE-1 zeolite based proprietary catalyst)*
Phenol, Acetone, Alphamethylstyrene*
High selectivity Cyclohexanone
Acetone hydrogenation to Isopropyl Alcohol*
Isopropyl Alcohol to Cumene**
Ammoximation (with Titanium silicalite based proprietary catalyst TS-1)

DMC and derivatives

Dimethylcarbonate (via Carbon Monoxide and Methanol)*
Diphenylcarbonate*

Proprietary catalysts

Titanium silicalite
PBE-1 Zeolite
PBE-2 Zeolite

Styrenics

Ethylbenzene (with PBE-1 and PBE-2 zeolite based proprietary catalyst)
Styrene
GPPS
HIPS
EPS suspension polymerization
ABS continuous mass polymerization
SAN

Polyethylene

LDPE
EVA

Elastomers

Emulsion-SBR
HSL Latices
Solution-SBR
TPR
LCBR
HCBR
NBR
Carboxylated latices
EP(D)M

* Co-licensing in cooperation with Lummus Technology (a McDermott International Company).
** Close to commercialization.

Versalis spa
Piazza Boldrini, 1
20097 San Donato Milanese (MI) - Italy
Ph. 0039 02 520.1

info@versalis.eni.com
versalis.eni.com

Responsible Care

Licensing:
Piazza Boldrini, 1
20097 San Donato Milanese (MI) - Italy
Ph. 0039 02 520.42931 - fax 0039 02 520.42286

info.licensing@versalis.eni.com

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