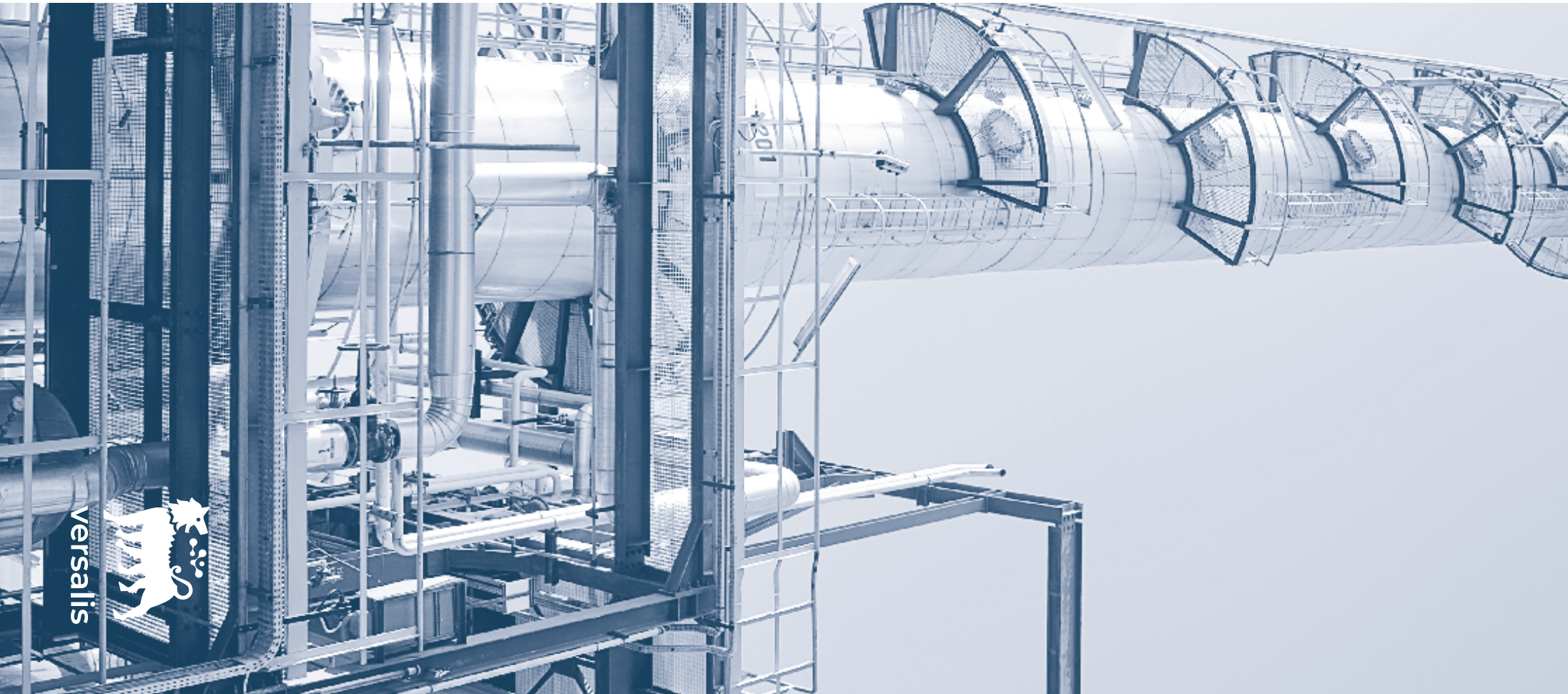
S-SBR

Solution Styrene-Butadiene Rubber copolymers



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 solution SBR technology

Solution polymerized styrene-butadiene rubber is the unrivalled raw material for highly specified tyre components used in the fabrication of high performance tyres, where the lowest fuel consumption and the highest durability are required.
The wide product portfolio allowed by the Versalis technology can be then used for fabrication of special tyre threads showing enhanced wet grip performance, as well as for fabrication of winter tyres and special mechanical goods. Depending on desired product and application, batch and continuous polymerization process are available in Versalis solution SBR technology. S-SBR proprietary technology has been developed as an alternative to emulsion technology to produce new product grades and also to greatly reduce some environmental impact of the emulsion technology.

Main technology highlights are:

- large production flexibility due to availability of both batch and continuous polymerization technologies, whose selection is driven by the final application of the product;
- cyclopentane, cyclohexane or n-Hexane or blend highly compatible with all different polymer compositions, can be used as solvent depending on local climate conditions;
- high and medium vinyl grades as well as Dry and Oil Extended polymers are allowed;
- production of polymers with linear radial or branched different macrostructures;
- process design advanced features in polymerization and purification sections;
- small quantity of volatile organic compounds (solvent) entering finishing section (low release during extrusion);
- optimized configuration of the stripping section with three stages arrangement to minimize steam consumption without impacting emissions of voc.

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 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 S-SBR technology allows to provide with a single line a fairly broad range of economically feasible capacities: up to 65 kt/y per reaction unit, up to 40 Kt/y per finishing line (batch grades), up to 45 kt/y per finishing line (continuous grades).

Wastes and emissions

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). Some selected exhaust streams from finishing section are usually sent to a regenerative-type thermal oxidizer (ISBL) in order to minimize the environmental impact of the process. Normal process venting are collected and can be sent to flare or other OSBL systems.

Industrial applications

First production line was built in Grangemouth (UK) in 1995, based on batch process technology and having a capacity of 30 kt/y, followed in 1999 by a new reaction section based on continuous polymerization process technology.
A third unit, based on 100 kt/y capacity with continuous and batch polymerization lines, has been licensed in the Far East and is on stream since 2009.
Two further plants in the Far East are on stream since 2017 (a batch one with a capacity of 40 kt/y and a continuous one with a capacity of 60 kt/y).
Another plant, based on batch technology (60 kt/y) has been licensed in Middle East and is currently under construction.

Main process parameters

	per MT of S-SBR
Raw Materials (Butadiene, Styrene, Aromatic Oil)	1,003 kg
Electricity - Continuous Process	0.56 MWh
Electricity - Batch Process	0.6 MWh
Steam (Medium Pressure + Low Pressure[1])	5.5 MT

[1] 10 barg and 6 barg respectively.

The Europrene® S-SBR copolymers product portfolio

The Versalis S-SBR technology enables the production of many grades of Dry and Oil Extended polymers through batch or continuous polymerization. Tuning the polymer composition (% of styrene) and polymer microstructure (% of vinyl group) is possible to obtain products, in the field of tyre application, characterized by:

- good processability;
- good ice/snow grip;
- good rolling resistance;
- grades with optimum compromise between rolling resistance and grip.

The tyre main applications of Versalis S-SBR grades are:

- silica based compound for H/V tread;
- ultra High performance tyre tread;
- silica based compound for H/V tread winter.

Such portfolio of products is continuously improved by our R&D centers through tyre manufacturers feedback. All polymer grades are stabilized with a specifically designed antioxidant package.

Process description

Solution polymerized styrene-butadiene rubber is obtained by anionic copolymerization of styrene and butadiene initiated by lithium alkyls in paraffine or cycloaliphatic solvent; due to the large difference of reactivity ratios for the two monomers, addition of a living chain-end modifier changing the above-mentioned reactivities is required to obtain a well randomized copolymer.

The rubber macrostructure can be efficiently managed/driven by a proper selection of polymerization type (batch, continuous), reaction conditions and suitable coupling or branching agents, greatly enhancing the final properties of vulcanized rubber. It is worth to note that the long chain branching, due to radical reactions forming high molecular weight arms, is a competitive advantage of Versalis technology. The elastic properties of the uncured rubber are then greatly modified, allowing an easier incorporation and dispersion of the fillers.

The process is first based on the purification of solvent and monomers through distillation and adsorption operations as well as blanketing with dry nitrogen of all chemical mix and feed tanks, in order to ensure the lowest level of poisons detrimental to polymerization reaction.

Dry solvent (n-hexane or cyclopentane), styrene, initiator, butadiene and other reactants are continuously loaded to the polymerization reactor train or charged batchwise in a specified sequence to the batch polymerization reactors, depending on grades to be produced. Reaction temperature control is enabled by the use of boiling reactor while the using of proper randomizing agent ensures a complete randomness of styrene with the desired level of vinyl unit.
The polymerization conditions lead to a practically complete depletion of monomers; at the end of polymerization the living chain ends are terminated by addition of substances which modify the polymer structure; so radial or branched or linear rubber can be obtained in order to match the required properties.
After polymerization completion the solution is then pumped to a blend tank operating at slight pressure.
Residual traces of unconverted monomers, together with a portion of the solvent, are flash vaporised, condensed and then recycled to the wet solvent tank, while the concentrated polymer solution is blended in the blend tanks.
The blended solution with the antioxidant agents is fed to the stripping section where the solvent is removed by steam distillation in the presence of a dispersing agent aimed to control the crumb size in the slurry.
The vapours obtained from the stripping section are condensed and the solvent, separated from water by a decanter, is sent to the wet solvent tank.
The crumb slurry is then pumped to the finishing unit, where the crumb is dewatered on a shaker screen, being the water partly recyrculated to the strippers and partly sent to waste water treatment. The dewatered crumbs are dried in two mechanical extruders in series, cooled with air, weighed and baled.

Process design advanced features

Versalis proprietary technology has been developed with a great attention to improve the random polymerization of monomers, the control of impurities level (through which very high molecular copolymers are obtained), the control of temperature (which in turn leads to a closer control of polymer microstructure), the reactor fouling (which is very critical for living polymerization carried out in continuous reactors) and feeding procedure.
The competitiveness of Versalis proprietary technology is based on the following main key-points:

- relevant savings in term of steam consumption due to aliphatic nature of solvent, which in turn also leads to improvements in environmental health;
- relevant reduction in investment cost due to carrying out the reaction adiabatically or in temperature rise control which also allows easier reaction control as well as saving in energy consumption;
- large production flexibility due to availability of both batch and continuous polymerization technologies, whose selection is driven by the final application of the product;
- high and medium vinyl grades as well as Dry and Oil Extended polymers are allowed;
- special purification section brings raw material impurities to negligible level, avoiding detrimental effects on both the process and structural parameters of the product;
- perfect randomization of styrene in polymer chain is allowed by the proper use of substances which modify the leaving chain ends;
- production of different grades of S-SBR ranging from low styrene-low vinyl to high styrene-high vinyl grades is allowed, based on both batch or continuous processes;
- production of polymers with different macrostructure: linear, radial or branched, being the latter a unique plus of our proprietary technology.

fig. 1

Batch S-SBR • process scheme

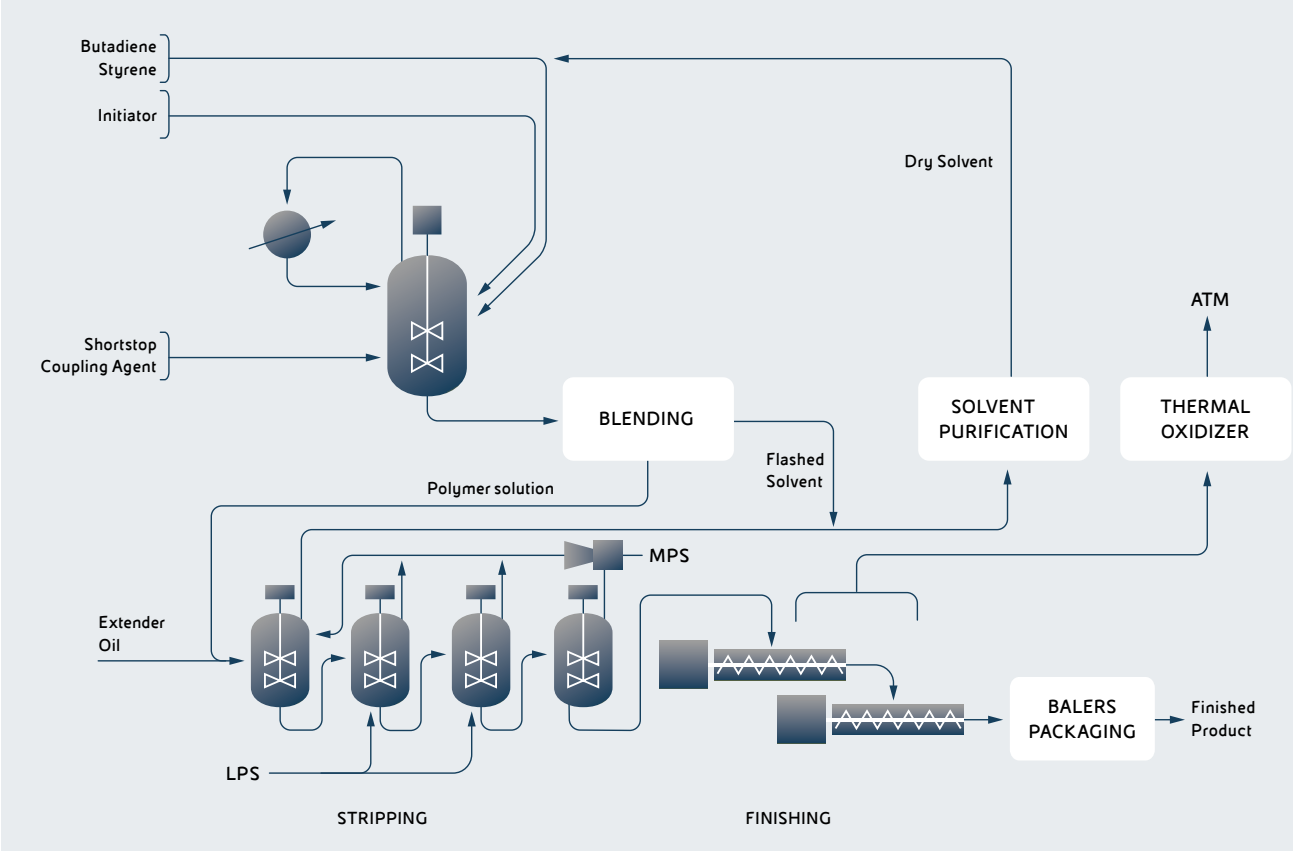
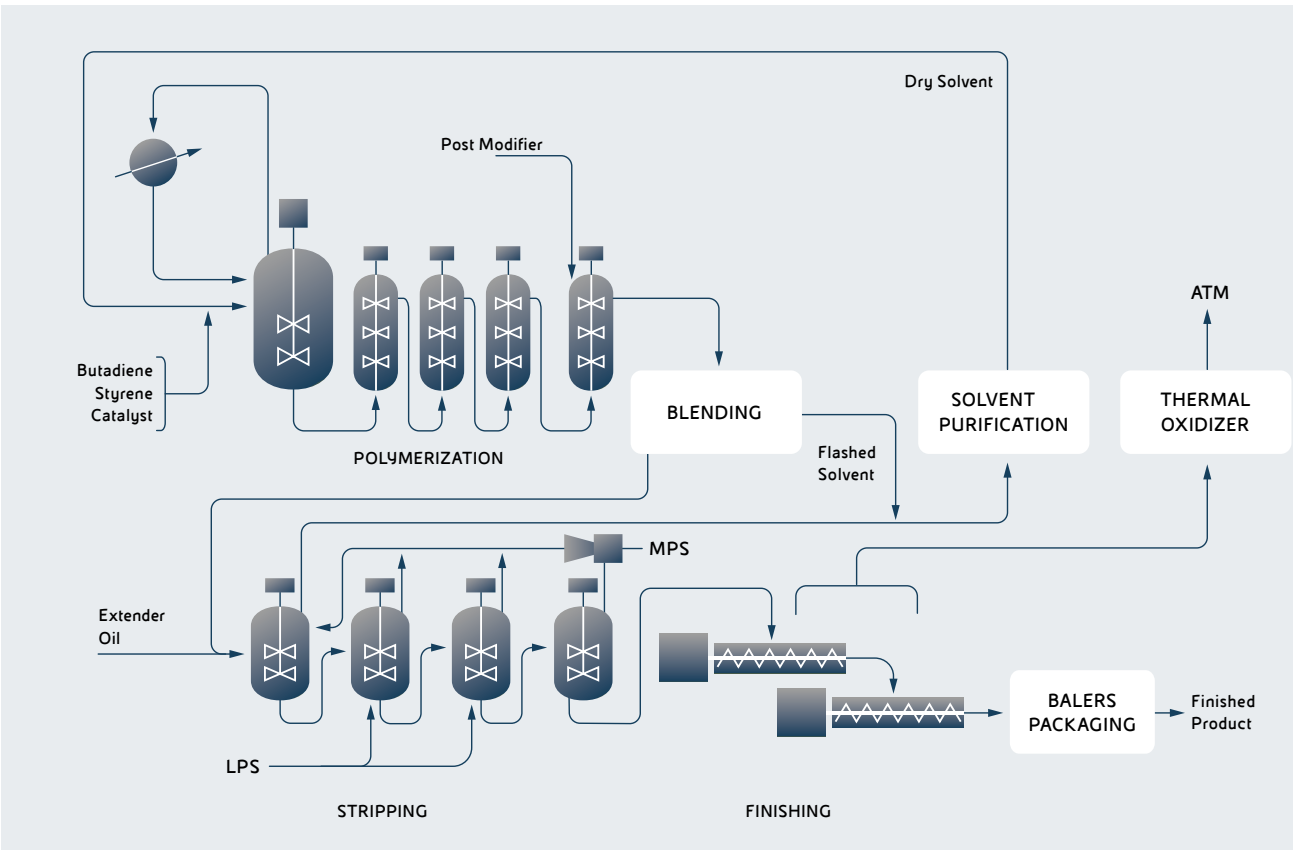


fig. 2

Continuous S-SBR • 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.

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