E-SBR

EMULSION STYRENE-BUTADIENE RUBBER COPOLYMERS

versalis

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 emulsion SBR technology

Emulsion polymerized styrene-butadiene rubber is one of the most worldwide used polymers, employed in a large variety of applications which significantly contribute to our standards of living as well as in enhancing our quality of life.
The unusually wide range of products achievable by the Versalis proprietary technology covers all e-SBR field of application like tires, footwears, light coloured mechanical goods, flooring adhesives, pharmaceutical and food contact articles, microcellular articles, hoses, conveyor belts, high hardness soles and sheeting, technical goods with high hardness. Versalis can offer Hot Latices technology (semibatch) whose products are blendable with e-SBR Latices giving High Solids Latices (HSL) and High Styrene Resins (HSR) materials with increased styrene content.

Key features of Versalis E-SBR production technology are:

- wide range of products grades, coupled with a real process know-how, enables meeting the specific needs of the customer;
- high flexibility allowing production, in the same continuous reactors train, of base Latices blendable with batch or semibatch latices to produce a HSR/HSL grades and SBR latices;
- great attention to environmental issues in design of each process stage, according to the BAT and to the IISRP suggestions to the E.U. Authorities;
- high polymerization conversion that reduces monomers and utilities consumptions leading to both high productivity and process capability;
- lower dimensions of recovery section leads to lower capital investment;
- high reliability and less downtime due to proprietary design of cooling system (coils and agitation) system;
- low concentration of the residual VOC content in the exhaust (no thermal oxidizer installation is required).

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 and agitators. 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 E-SBR technology allows to produce with a single line a fairly broad range of economically feasible capacities: up to 75 kt/y per reaction unit with a single finishing line capacity ranging from 30 to 40 kt/y depending on product mix.

Wastes and emissions

The process produces oily waste water which can be treated in a normal bio-treatment.
Large waste air emission from finishing lines does not require any treatment due to its low concentration of pollutants. Normal process venting are collected and can be sent to flare or other OSBL systems.

Industrial applications

Versalis is one of the major industrial producer of Emulsion SBR in Europe with an industrial unit located in Italy. Such a plant is on stream since 1957 based on a 120 kt/y capacity.

SBR latices, low and high solids, are produced in Italy based on a 25 kt/y capacity, on a dry basis. HSR (High Styrene Resins) are also produced in Italy.

One Emulsion unit (141 kt/y) has been recently started up in India, while another one (136 kt/y) is under construction in Middle East, both licensed by Versalis.

Main process parameters

	per MT of oil extended E-SBR
Raw Materials (Butadiene[1], Styrene [1], Aromatic Oil)	970 kg
Electricity[2]	0.4 MWh
Low Pressure Steam[2]	2.4 MT
Cooling Chilled Water (ΔT + 8 °C)	350 m³

	per MT of dry E-SBR
Raw Materials (Butadiene[1] + Styrene [1])	955 kg
Electricity[2]	0.5 MWh
Low Pressure Steam[2]	2.6 MT
Cooling Chilled Water (ΔT + 8 °C)	400 m³

[1] Value includes reject butadiene and styrene which could be recovered reducing the net specific onsumption.
[2] Expected consumption related to standard Plant configuration, including ammonia refrigerating unit, chilled water production and waste water pre-treatment, standard monomers purities and mild Site climate.

The Europrene® E-SBR copolymers portfolio

Emulsion SBR product is available in a range of Mooney viscosities, with 1500 series displaying some properties like easier incorporation of fillers and oil, less heat generation during mixing, higher extrusion rates and extrudate superior appearance, while 1700 series have better green strength and higher acceptance of filler and oil loadings.

Increase in molecular weight strengths the vulcanizate resilience and mechanical properties, while SBR processability improves when molecular weight distribution broadens. Processability is also affected by polymerization temperature, leading to less chain branching at low temperature compared to the high temperature.
The emulsifier system also affects rubber properties, as polymer emulsified with 100% Rosin acid gives better extrusion rates, slower cure rates and higher tack of the green compound while the use of 100% Fatty acid gives faster curing and high tensile properties.
The emulsifier system is then usually a blend of Fatty and Rosin acid.

Main application of oil extended types (1700 series) and dry types (1500 series) are tyres, retreading, conveyor belts, hoses, footwear, flooring, sheeting, adhesives, carpet underlay, microcellular articles and coloured and calendered goods.

Process description

Styrene and butadiene monomers polymerize in the presence of an emulsifier (fatty or rosin acid soaps), an initiator system, a modifier (mercaptan) and water.
Initiator agent in case of cold polymerization is the redox reaction between chelated iron/organic peroxide and sodium formaldehyde sulfoxilate as reducing agent.
The molecular weight distribution is primarily controlled by addition of mercaptan which terminates the growing chains beside initiating the new ones.
Polymerization takes then place at the mild conditions typical of emulsion polymerization, controlling at the same time the reactants flowrate up to the addition of the shortstop agent – when desired conversion is reached – which rapidly reacts with free radicals blocking reaction.

The Versalis E-SBR technology is based on an isothermal continuous polymerization carried out through a series of reactors up to the desired reactants conversion is reached. Butadiene and styrene monomers and demi water are first emulsified and pre-cooled, then solutions of catalyst, modifier and activator are added to the mixture before entering the first reactor.
Each reactor is equipped with a distinctive and original design of evaporating ammonia cooling coils that allows both the selection of polymerization temperature according to the desired product grade and an effective chemical cleaning (less downtime and environmental impact).
Reaction is stopped in the last working reactor by shortstopper addition (catalyst & chemicals used are all available in the open market).
The emulsion is then discharged into latice blow down drums and unreacted butadiene is recovered through a two steps flash – the first one at atmospheric pressure and the next one under vacuum – submitted to compression and condensation and then recycled to the monomer storage section.
Latice is first pumped to the styrene stripping tower – where unreacted styrene is recovered by direct injection of L.P. steam – recovered as bottom product and then pumped to finishing section.
OVHD vapours are condensed and sent to the water/styrene decanter.
Styrene is first cooled and then recycled to recycle styrene tanks.

The uncondensed vapours, containing mainly butadiene, are sent to liquid ring vacuum pumps to be recovered while water from decanter is fully recycled to reaction, greatly reducing the environmental impact of the process.

Storage and blending tanks for latice display sufficient hold up to allow stopping the finishing section when product grade changes. Finishing section is then fed by latice, antioxidant and extended oil (in case) which coagulate in a series of stirred vessels with a vibrating screen which separates rubber crumbs from water, sending them to the washing tank and then to the dewatering unit. Water content in SBR is reduced by means of a continuous hot air belt dryer (Apron dryer) where air is moved in by means of blowers.
The rubber is then fed to the balers.

Process design advanced features

- High polymerization conversion that reduces monomers and utilities consumptions leading to both high productivity and process capability.
- High reliability and less downtime due to proprietary design of cooling system (coils and agitation) system.
- Lower dimensions of recovery section leads to lower capital investment.
- Rejected monomer quantity is reduced thanks to a specific section design, integrated with upstream plants, allowing reduction of slop quantity.

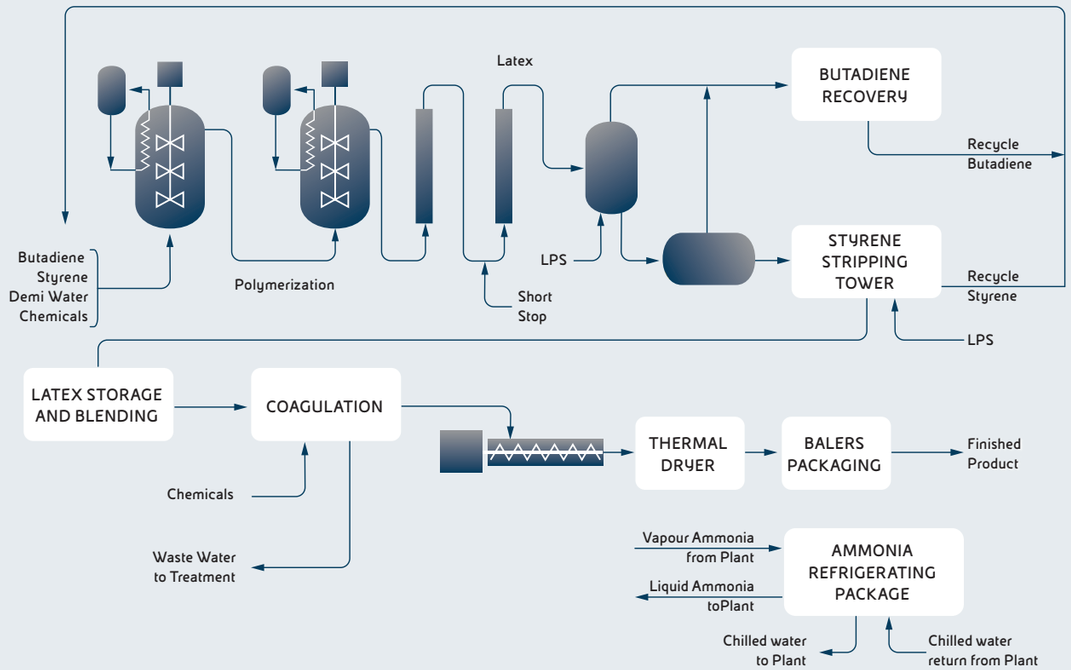
Versalis is able to design this recovery section based on both client needs as well as site conditions.
Possible technical options for the unreacted butadiene-rich stream (BD reject) are the recycle to butadiene extraction unit or C4 feedstock under technical conditions which are included into Versalis Know-How or LP steam generation.
The unreacted styrene-rich stream (styrene reject) under technical conditions which are included into Versalis Know-How, can be fed to a styrene monomer plant in order to recover 95 - 98% of the styrene content of the stream.

All the enviromental issues coming from gaseous effluents, liquid effluents, water consumption and solids effluents have been deeply considered in the design base of each process stage, according to the best available technologies as well as to the IISRP suggestions to the E.U. Authorities.
Significative examples are given below:

- **Water recycle**:
  all the watery phase recovered after the latice stripping are recycled to reaction, water streams from reaction or monomer recovery to CWWT are pre-treated with a dedicated steam stripping section.
- **VOC captation:**
  vapour streams from reaction and recovery areas are connected to flare or other OSBL systems also for maintenance operations (low emission factors).

fig. 1

E-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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