Proprietary process technology

SBS

Styrene-Butadiene-Styrene block copolymers

eni 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 SBS technology

SBS copolymers, made by styrene and butadiene linked homopolymer blocks, belong to the class of thermoplastic elastomers (TPE), whose elastic behaviour - the properties to change and recover the shape when a force is first applied and then removed - and thermoplastic behaviour - the property to become soften, viscous and free-flowing like a liquid when heated and return solid when cooled at room temperature - are joined together in the same material.
The elastic/rubbery and thermoplastic/viscous behaviours are displayed at room and high temperatures respectively allowing the fabrication of TPE goods having the same rubbery feeling than traditional vulcanized rubbers, but considerably less expensive in manufacturing process due to the full recyclability of scraps, the shorter cycle, time and the easier process automation/robot assistance.
This balance between properties and processability leads SBS based material focusing on unique applications instead of only replacing general-purpose rubber. Versalis SBS technology is well-known for its high flexibility in tailoring the different product grades required by the SBS market which is characterized by a continuous product innovation to meet new application requirements. Versalis SBS technology allows then competitive production of the most common SBS grades, as well as additional grades for special applications.
Key features of Versalis SBS production technology are:

- high flexibility in terms of product mix and good quality constancy and reproducibility;
- high plant capability as well as easy operability due to both specifically designed feeding system for chemicals and batch automation;
- cyclopentane, cyclohexane or blend highly compatible with all different polymer compositions can be used as solvent depending on local climate conditions;
- high purity linear and radial triblock polymers, with four arms, are allowed by the proper selection of halosilane structure as coupling agent;
- production in the same unit of Low Cis Butadiene Rubber (LCBR) grades and/or SB (diblock styrene-butadiene polymers) used mainly for plastic modification or tyre market is possible;
- process design advanced features in polymerization and purification sections;
- 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 (solvent) 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 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 SBS technology allows to provide with a single line a fairly broad range of economically feasible capacities: up to 50 kt/y per reaction unit, up to 30 kt/y per single finishing line.

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

Versalis is currently one of the major industrial producer of SBS polymer. Three industrial units worldwide, in Italy, Far East and US, are currently based on proprietary SBS technology. Another unit is under construction in the Mid East Area. The Italian plant is on stream since 1970 based on a current 90 kt/y capacity, which has been reached throughout two plant revampings, in 1991 and in 2001.
The US plant is on stream since 1992 based on a current 45 kt/y capacity; since 2003 this plant is no longer property of Versalis. The Far East plant has been recently set on stream (2009) and is based on a current 80 kt/y capacity. A fourth unit (based on 30 kt/y capacity of SBS and 30 kt/y of SB/LCBR) has been licensed in Middle East and is currently under construction.

Main process parameters

	per MT of oil extended SBS
Raw material (Butadiene + Styrene + Paraffinic oil extensor)	1,010 kg
Electricity	0.55 MWh
Steam (medium pressure + low pressure[1])	5 MT

	per MT of dry SBS
Raw material (Butadiene + Styrene)	1,010 kg
Electricity	0.5 MWh
Steam (medium pressure + low pressure[1])	5.5 MT

[1] 10 barg and 6 barg respectively.
Expected consumption related to standard Plant configuration, solvent Cyclopentane, mild site climate, air cooling applied where possible.

The Europrene® SBS block copolymers portfolio

Material properties are mainly dictated by the ratio between polystyrene and polybutadiene amounts as well as by the molecular weight of the homopolymer blocks. At microscopic scale, low styrene content elastomers show a morphology of polystyrene spheres with dimensions of 300-350 angstrom dispersed in a rubbery matrix while the progressive increase of styrene content leads polystyrene spheres to change into cylinders and then into lamellae. A further increase in styrene content turns the material into a plastic matrix in which the dispersed elastomer gradually changes from cylinders up to spheres. The material then behaves as a vulcanised elastomer at low styrene content, when the elastomeric phase is the continuous one, while impact resistance properties predominate at low butadiene content, when the polystyrene phase becomes the continuous one.

A proper pre-definition of both molecular weights and molecular weight distribution of the blocks, as well as their purity, avoids the progressive worsening of the mechanical characteristics due to poor phase separation.

The Versalis proprietary SBS technology allows the production of many grades of Dry and Oil Extended polymers, mainly characterized by a different percentage of styrene block as well as by different linear or radial molecular structures.

Such portfolio of products is continuously improved by our R&D centers through market feedback. All polymer grades are stabilized with a specifically designed antioxidant package. Versatile tuning of final product properties can be easily obtained by mixing with other polymers, oil and fillers allowing wide product applications, ranging from enhancer of bitumen performance in road paving and roofing applications (particularly under extreme weather conditions), through adhesives, sealants, coatings, footwear up to compounds able to enhance grip, feel, and appearance properties in toys, automotive, personal hygiene, and packaging goods market.

Process description

Styrene butadiene triblock copolymers are obtained by anionic polymerization initiated by lithium alkyls in cycloaliphatic media as solvent; main features of this class of anionic chain polymerization is the livingness, i.e. the ability of polymeric chain ends to survive even when monomer is completely depleted and to reinitiate the polymerization reaction when monomer is newly added. Due to the absence of termination reactions, polymer active chain-ends do not inherently terminate, continuously growing up to the complete monomers depletion, which in turn means that average polymer molecular weight can be really predicted from the amount of starting material and the quantity of initiator.
Flexibility is the peculiar aspect of this polymerization technique which allows, under appropriate conditions, the production of thermoplastic elastomers differentiated by composition (in styrene), molecular weight and structure, ranging from pure triblock, both linear and star copolymers, to tapered diblock.
Three main synthetic methods are employed. In the two stages polymerization the living styrene-butadiene diblock copolymer becomes a linear triblock SBS copolymer by subsequent addition of a difunctional coupling agent, whose relative amount can be varied to obtain different yields of coupled SBS and uncoupled SB polymers.

Alternatively the addition of a coupling agent having a functionality of three or more leads to the formation of radial block SBS copolymer, whose number of SB arms depends on the structure of the polyfunctional coupling agent. When styrene is added instead of the coupling agent we refer to SBS three stages polymerization leading always to linear SBS copolymer. Finally a terminating agent must be added in order to terminate the active chain-ends.

The chemical residuals from terminating or coupling reactions must be inactive towards antioxidant in order to avoid yellowness of SBS copolymer.
Based on the above it comes that linear SBS can be obtained from both the three stages polymerization process as well as from the two stages one, while radial SBS can be only obtained from the two stages polymerization process.
When polymerization reaction of butadiene and styrene is carried out at the same time in batch reactor, a SB type copolymer is obtained. In this case polybutadiene and polystyrene blocks join together through a portion of polymeric chain (tapered junction) in which a progressive variation of composition is observed.

The consequent lack of the second block of polystyrene does not allow the mechanical properties of pure triblock copolymers, but enhances other useful properties for adhesives applications and bitumen modifications.

Dry solvent (cyclohexane or cyclopentane), styrene, initiator, butadiene and coupling/ terminating agent are loaded batchwise to the polymerization reactor, based on a sequence defined by a specific procedure depending on type of polymer to be produced.

Solvent and monomers distillation and adsorption operations before loading, as well as blanketing with dry nitrogen of all chemical mix and feed tanks, keep impurities at the lowest level, preventing polymerization poisoning. When polymerization reaction is completed, the polymer solution is pumped to a blend tank operating at slight pressure.
Portion of solvent together with unreacted monomers are flash vaporised.

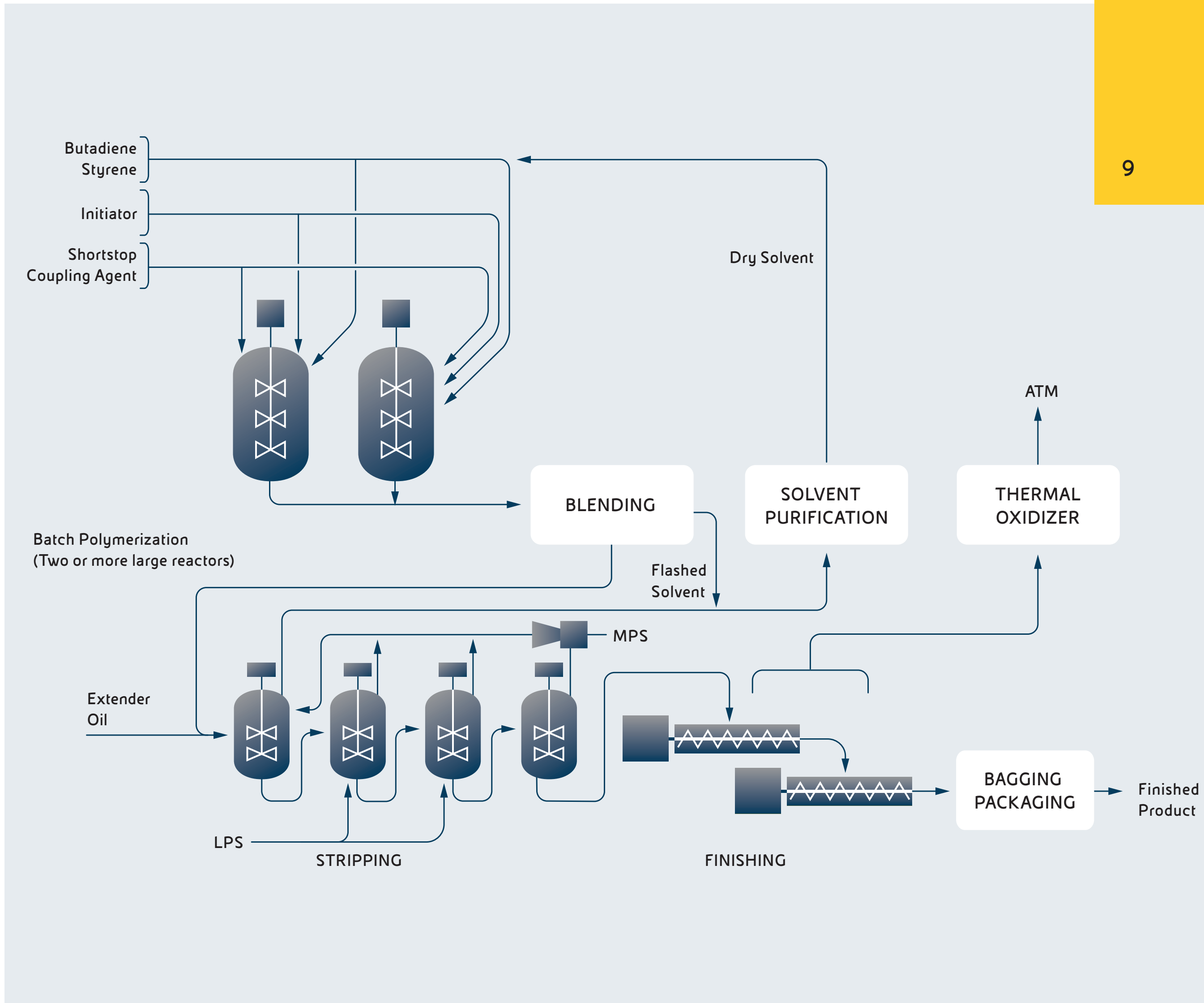
The vapours are condensed and recycled to the wet solvent tank.
The blended solution with the antioxidant agents is fed to the stripping section where the solvent is removed by steam stripping in the presence of a dispersing agent for controlling the crumb size.
The vapours leaving the stripping section are then condensed and the solvent, separated from water in a decanter, is sent to the wet solvent tank. The crumb slurry is pumped to the finishing unit, where the crumb is dewatered on a shaker screen, from which water is partly recirculated 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 finally bagged.

Process design advanced features

- High reactor volume (about 50 m³) and capacity up to 50 kt/y for single reaction line, lowering the investment cost;
- special design of solvent and monomer purification columns allows the removing of light and heavy components by one equipment;
- cyclopentane, cyclohexane or blend, highly compatible with all different polymer compositions, can be used as solvent depending on local climate conditions;
- proper solvent/monomer ratio in batch polymerization beside a defined solvent blend lead to lower steam consumption in stripping operation. Up to 30% saving in steam consumption by using cyclopentane instead of cyclohexane;
- special design of die plate in dryer system and proper operating condition lead to regular shape of crumb rubber with different density;
- high purity linear and radial triblock polymers, with four arms, are allowed by the proper selection of halosilane structure as coupling agent;
- high plant capability as well as easy operability due to both specifically designed feeding system for chemicals and batch automation;
- proper selection of antioxidant package as well as of packaging material avoids damages to the marketed crumb or powder final product, even if incorrectly stored.

fig. 1

SBS • 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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