Proprietary process technology

# LCBR

Low Cis Polybutadiene Rubber polymers

# 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 LCBR technology

Versalis Low Cis Polybutadiene rubber (LCBR) was developed by Eni in the 80s with the aim to produce rubber grades with specific properties in industrial applications. Due to the low quantity of 1,4-cis unit (< 50%) this type of polybutadiene is indicated as LCBR in front of HCBR obtained with metal coordinate polymerization. The main use of LCBR is in the production of High Impact Polystyrene (HIPS) and Acrylonitrile ButadieneStyrene (ABS). It would also be an interesting material for modulating the properties of a compound for a tyre tread. Polybutadiene prepared through anionic polymerization, because of the narrow molecular weight distribution is known to show the cold flow phenomenon, which translates into dimensional instability of the bales in which it is packaged. Polymerization conditions adopted in Versalis process induce the formation of a minority fraction of long chain branched polybutadiene that greatly modifies the rheological behaviour of the material; geometrical constancy of the bales is then guaranteed. Key features of Versalis LCBR production technology are:

- high flexibility in terms of product mix and good quality constancy and reproducibility;
- Versalis is able to design a Plant for the combined production of continuous LCBR and S-SBR grades using the same reaction line, thus significantly reducing the investment;
- all the grades can be stabilized with an antioxidant system that has food contact approval;
- polymerization reaction is carried out adiabatically bringing many advantages concerning energy consumption, investment cost and easier operations. Furthermore the problems of products quality that would arise in case of troubles in removing the polymerization heat are then avoided;
- 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);
- process design advanced features in polymerization and purification sections.

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 LCBR technology allows to provide with a single line a fairly broad range of economically feasible capacities: up to 60 kt/y per reaction unit, with capacity up to 36 kt/y per 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). 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.
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

The first production plant (50 kton/year) is on stream since 80s at the Versalis site in Grangemouth (UK).
In 2009 a new continuous combined LCBR/s-SBR line was set on stream for an installed capacity of 60 kt/y in the Far East as part of a larger project which includes batch LCBR, batch BR and SB grades, SBS and batch S-SBR grades. Two further combined 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 LCBR |
|---|---|
| **Raw Materials** (Butadiene) | 1,01 kg |
| **Electricity** | 0.6 MWh |
| **Steam** (Medium Pressure + Low Pressure[1]) | 5.2 MT |

[1] 10 barg and 6 barg respectively.

# The Europrene® LCBR polymers portfolio

It is well known that a brittle plastic material has a tendency to fracture when it is deformed. Well dispersed particles of rubber inside the plastic matrix are able to reduce this phenomenon. Versalis produces many grades of LCBR suitable for this application.

LCBR are characterized by the following properties:

- high consistency;
- high purity;
- low cold flow;
- low gel content;
- low dissolution time in styrene;
- wide range of solution viscosity;
- low glass transition temperature.

Versalis LCBR grades cover different solution viscosities in the range 80-270 cPs.
Main application of LCBR polymers are tyres, belting, moulded and extruded articles and production of High Impact Polystyrene (HIPS) and Acrylonitrile Butadiene Styrene (ABS) grades.



# Process description

The LCBR polymers are obtained by anionic polymerization initiated by lithium alkyls in aliphatic/cycloaliphatic media (n-hexane or cyclopentane) as solvent. The lithium alkyl initiated polymerization of dienes belongs to the class of anionic living polymerization whose typical feature is the absence of any termination reactions (living polymerization); this gives a polybutadiene with vinyl content < 10%, trans and cis being quite of the same quantity, with a narrow molecular weight distribution (Mw/Mn < 2,2). The reaction is carried out using one agitated continuous reactor.
Due to the features of anionic polymerization in continuous reactors the use of an antifouling agent is necessary in order to prevent any gel formation during the polymerization. Antifouling is an hydrocarbon which is continuously fed in reaction in a fixed ratio with initiator. The main feed stream for the LCBR reactor lines is a mixed feed of solvent and butadiene which is pumped into the reactor area, to the base of the peak reactor, along with a dilution solvent flow, initiator and antifouling. The reaction is exothermic and the heat evolved is absorbed by the reactor contents, raising their temperature to the required value.
The reaction takes place at a constant pressure sufficient to keep the 1,3 butadiene in the liquid phase and available for the polymerization reaction through the use of a back pressure control valve situated in the product line leaving the reactor.
The polymer solution then passes into the flash reactor where the high temperature and reduced pressure causes some of the solvent to 'flash off'. This solvent vapour is extracted from the flash vessel, condensed and returned to the peak reactor as the aforementioned dilution solvent stream.
On leaving the flash reactor, the cement passes through mixers, to which shortstop and antioxidants are mixed, before it passes to the Blending section.
The blended solution 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 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 vapours obtained from the stripping section are otherwise condensed and the solvent, separated from water by a decanter, is sent to the wet solvent tank.
The dewatered crumbs are dried in two mechanical extruders in series, cooled with air, weighed and baled.

# Process design advanced features

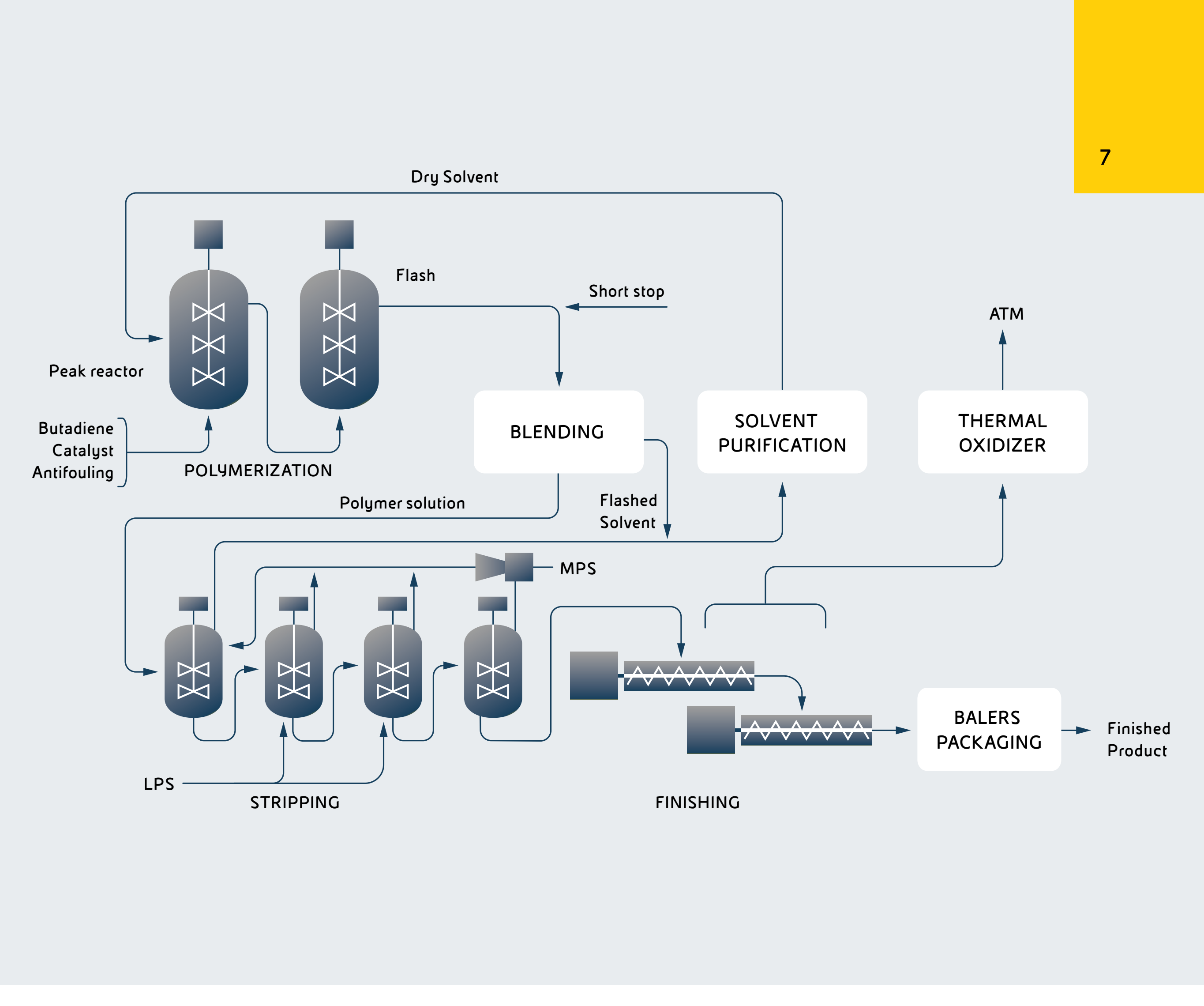
Versalis proprietary technology has been developed with a great attention to improve the product quality by means of a considerable control of impurities level, the reactor fouling (which is very critical for polymerization carried out in continuous reactors) in terms of operation and frequency.
The competitiveness of our proprietary technology is based on the following main key-points:

- high reactor volume per reactor unit, thus allowing high plant capacity;
- pressurized blending section instead of atmospheric tanks: safer operating condition;
- configuration of the stripping section: three stages arrangement optimized in such a way to minimize steam consumption without penalizing emissions of hydrocarbons from finishing line to the atmosphere;
- during the process solvent becomes wet and impure. Distillation is needed for drying solvent and to remove these undesired impurities. In Versalis Technology particular attention is paid to avoid polymer presence in wet solvent fed to the column;
- cyclopentane, n-Hexane or blend highly compatible with all different polymer compositions can be used as solvent depending on local climate conditions;
- very good control of impurities level through a special design in purification section that leads to market required product quality;
- special design of continuous and adiabatic section in order to minimize reactors fouling, to lower investment costs and to save energy;
- process is tuned in terms of solvent/monomer and solvent/rubber ratio in each stage of the process to optimise the heat balance and increase the solid content of the cement, thus reducing the utilities consumption;
- special purification section brings raw material impurities to negligible level, avoiding detrimental effects on both the process and structural parameters of the product.



fig. 1

LCBR • 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

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