

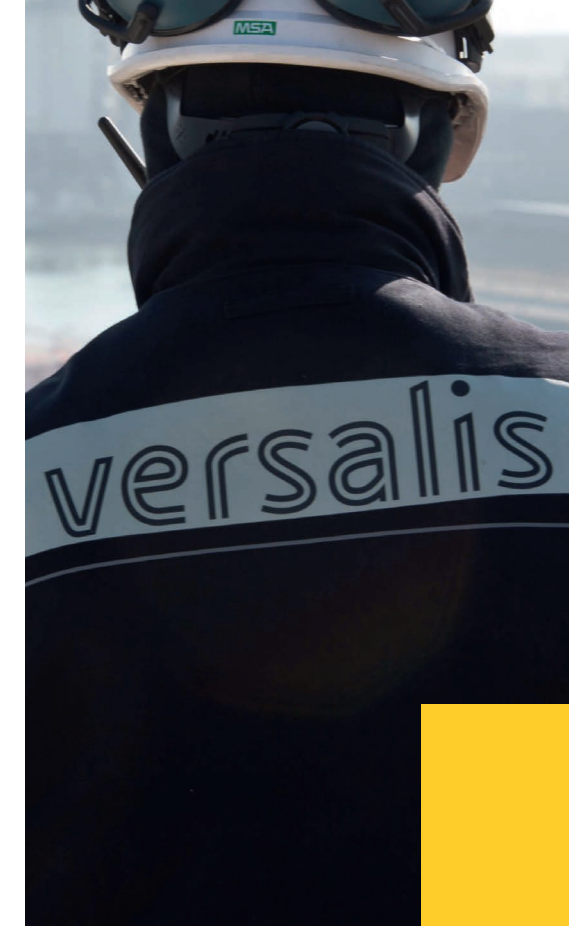
Proprietary process technology

ABS

Acrylonitrile Butadiene Styrene copolymers

CONTINUOUS MASS POLYMERIZATION TECHNOLOGY





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 ABS continuous mass technology

Versalis has been producing Acrylonitrile-Butadiene-Styrene plastic according to the traditional emulsion process since 1963. At the end of the 80s, Versalis started also the production of ABS based on an innovative continuous mass technology developed meanwhile by its R&D and already extensively used for HIPS and GPPS since the 70s.

In 2005, the production and sales of emulsion based products were completely stopped and Versalis decided to concentrate only on the continuous mass technology. The key features of Versalis ABS continuous mass technology are:

- superior lot-to-lot consistency, homogeneity and stability with respect to the traditional emulsion batch process;
- low environmental impact (no water used in the process, limited amount of vents containing VOC are generated by the process);
- minimum quantity of foreign materials introduced in the process, which gives rise "to clean" base material with respect to the emulsion technology and minimizes production costs;
- very low chemicals consumption for the same property balance (low formulation costs);
- very low residual monomer content in the product;
- flexible technology allowing tailor-made solutions for specific needs, in terms of plant capacity together with a fairly large range of grades;
- really simple process scheme which translates into low investment, maintenance and operating costs compared to emulsion technology;
- special and unique process and mechanical design of key equipment such as the reactor and devolatilizer;
- fine-tuned macromolecular structure (rubber particle size, resin molecular weight and its distribution);
- easy process control;
- patented heat recovery scheme to reduce plant energy consumption.

After a complete switch from emulsion to continuous mass process, Versalis is now in the position to offer a well balanced Sinkral® product portfolio, a benchmark within the global scenario.

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 Mantova since the early 70s, qualifies Versalis as an outstanding owner of know-how in the field of styrenics. Reliable and updated facilities (pilot plants, synthesis and analytical labs, equipment for polymer processing), allow Versalis to continuously improve the technology in order to support the styrenics business in a 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 fluidynamic analysis (CFD) are extensively applied to the design of key equipment such as reactors, agitators and devolatilizers. The design takes also advantage of the Versalis long-term manufacturing experience. New technological solutions are first tested in production plants; then the acquired experience is transferred to the licensed technology, in order to ensure not only the best process performances, but also a safe and reliable plant arrangement.



Mechanical design

Versalis Engineering Dept. has always been working in close coordination with the Process Dept. 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.

The flexibility of Versalis ABS continuous mass technology allows to provide with a single line convenient solution for a fairly large range of capacities: up to 80 kt/y.

Wastes and emissions

The main liquid organic wastes and vents are sent to a thermal oxidizer in order to comply with the most severe European and international standard for minimization of the environmental impact.

Industrial applications

Two Versalis ABS units, based on proprietary continuous mass technology, are on-stream in Italy (25 kt/y, since 1989; 45 kt/y, since 1991). One ABS unit (64 kt/y) licensed by Versalis has been recently started up in Russian Federation. One ABS unit (200 kt/y) licensed by Versalis is under construction in Middle East.

Main process parameters

	per MT ABS
Raw Materials	1,010 - 1,020 kg
Electricity	0.19 - 0.23 MWh
Fuel Gas (10,000 kcal/kg)	25 - 35 kg

The Sinkral® ABS product portfolio

The strengths of Versalis Sinkral® ABS, produced via continuous mass technology, are here summarised:

- "Clean" base material: as a consequence of the total absence of polymerization additives, the continuous mass ABS has an intrinsic light base colour but, more important, a greater stability of colour during final processing of the product.
- Higher thermal stability: being the continuous mass process a "clean" one, where no polymerization latex additives, soaps, emulsifiers etc. are involved, polymer degradation reactions are more difficult to occur.
- Lower volatiles content: the very low residual monomers content related to continuous mass process technology has, as a consequence, a very low emission of volatile molecules during processing and very low migration in food applications.

The flexibility of Versalis Technology allows to manufacture all main ABS grades, covering the following fields of application.

- **Medium and high impact**
Refrigeration, sanitary, transport, industrial packaging and furnishing profiles.
- **very high impact**
Extrusion of thick sheets for sanitary and transportation sector.
- **Ultra low gloss (matt surface)**
Extrusion/co-extrusion and matt furnishing profiles.
- **Injection moulding**
Very high flow, high gloss and toughness.
Small domestic appliances, toys and telephones.
- **High flow, high gloss, medium heat resistance**
Washing machines, dishwashers and electrical components.
- **High heat resistance**
Automotive industry, either for internal and external components.

Process description: from emulsion to continuous mass process

The commercial production of ABS started at the end of the 50s and, for at least two decades, it has been carried out via traditional emulsion process only. Emulsion process, being a discontinuous technology, while flexible and suited to the synthesis of specific materials (for example glossy ABS), is a much more intensive technology in terms of raw materials, chemicals and utility consumption. Furthermore, the complexity of the process scheme, which in most cases implies a synthesis of intermediates, impact significantly the investment, maintenance and operating costs.

In recent decades environmental issues have become more and more important and unavoidable in relation to the quality of the finished product (monomers and residual substances) and production features (quantity and quality of effluents, emissions in the workplace, etc.). The continuous mass production process does not use any raw materials or additives other than those used in the reaction (i.e. no water is needed in the reaction section) and thus allows a drastic reduction in the number and quantity of emissions. The simplified continuous mass ABS process scheme consists basically of a closed loop, single step technology. Raw materials are continuously fed and polymerized in the reaction section. The non reacted monomers/solvent are separated out from the polymer in the devolatilization section, condensed and recycled back to the reaction. The molten polymer is finally pelletized and sent to storage. Only a minimum amount of organic liquid purge discharge is necessary to remove impurities that can not be polymerized and non-polymerisable matters that otherwise would tend to accumulate.

The Versalis ABS technology is based on a continuous mass peroxide-initiated polymerization of styrene and acrylonitrile in a rubber-styrene solution.

Rubber, after being ground in a mill, is dissolved in styrene in a proper section and then fed with chemicals and co-monomer (acrylonitrile) to a downstream mixing section.

The mass reaction is carried out in the presence of solvent. This mixture is thus fed to the polymerization section, generally composed by a sequence of two/three plug-flow reactors; the reaction thermal profile is controlled by thermal oil circulating inside internal coils. The whole reaction section arrangement is selected case-by-case, in order to meet specific requirements.

At the end of reaction train, the polymer solution is sent to a devolatilizing section, consisting of two stages operated in sequence and under vacuum. The monomer, the co-monomer and low-boiling compounds are removed from the polymer, which is finally sent to the pelletizing unit. An additive is continuously admixed to the polymer before pelletizing.

The heat for process needs is provided by a thermal oil system.

The vapour mixture, after condensation, is continuously recycled to the mixing section. Noncondensed vapors/inert gases from the vacuum system and liquid organic purge from the condensation section are sent to a thermal oxidizer.



Process design advanced features

Versalis ABS technology is characterized by the following proprietary advanced design features:

Polymerization section

The main items are full plug-flow reactors (PFRs); thanks to agitation and a high specific thermal exchange surface area, they are characterized by very precise control of the thermal reaction profile. Any specific need in terms of product quality/portfolio can be matched by tuning the reaction train arrangement. In this way, it is possible to achieve maximum control of the morphology of the disperse phase, together with good efficiency of the catalytic grafting reaction. This synergy allows optimising the balance between production rate and polymer quality.

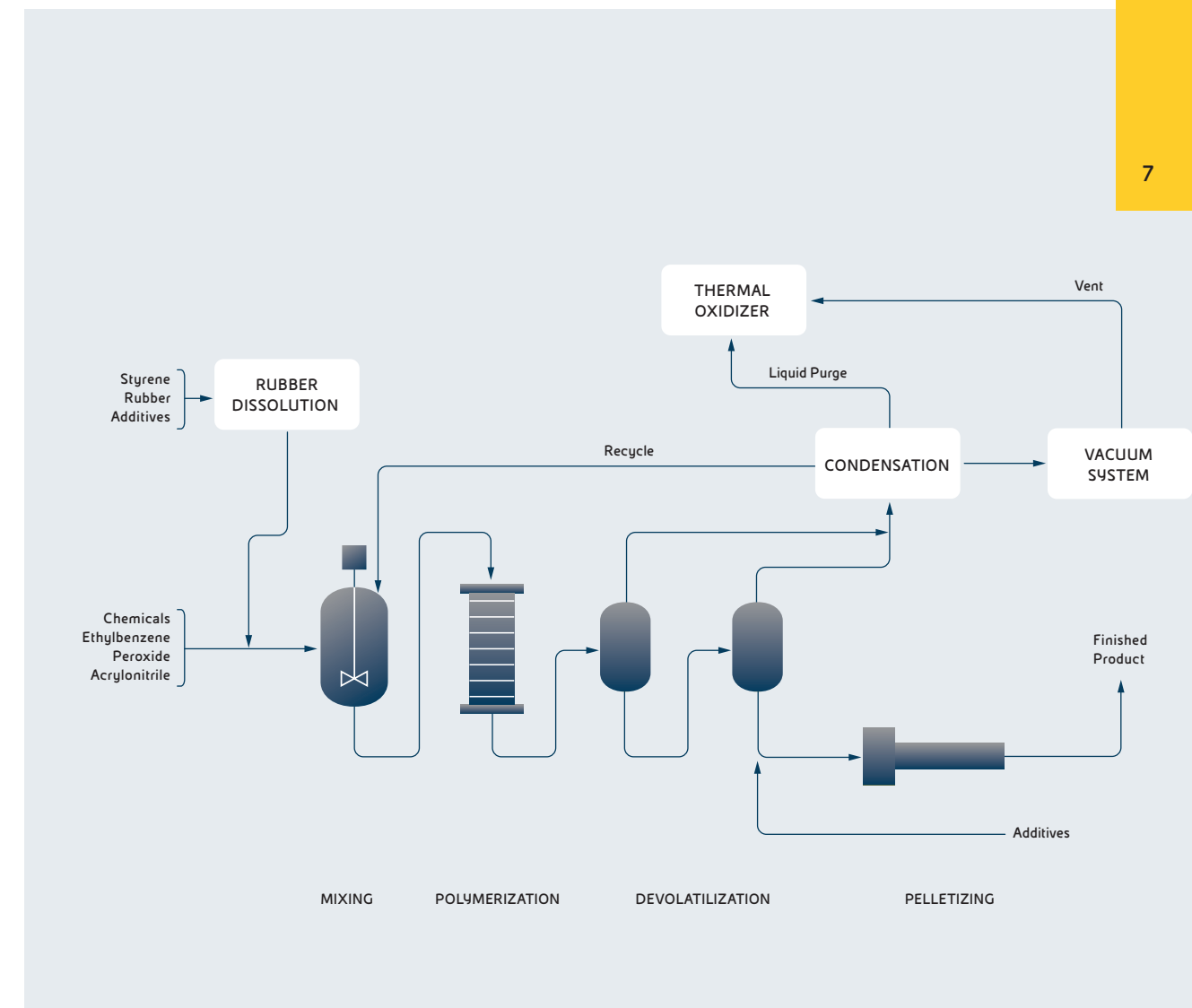
Devolatilization section

This involves two-stage operation, with high heat and mass transfer rates along with very low residence times. This combination of factors leads to a very efficient removal of monomer and organic matter even at relatively low temperature (thus minimizing polymer chain degradation and cross-linking of the rubber phase) and without the addition of water or other stripping agents.



fig. 1

ABS continuous mass • 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, Alkylphenols*
 High selectivity Cyclohexanone
 Acetone hydrogenation to Isopropyl Alcohol*
 Isopropyl Alcohol to Cumene**
 Ammoxidation (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



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

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



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



11 - 2018