



## s-SBR

Styrene-Butadiene  
random copolymers

Proprietary  
process technology



polimeri europa



## **POLIMERI EUROPA** PRODUCTION TECHNOLOGIES NOW AVAILABLE FOR LICENSING

### **Polimeri Europa**

Polimeri Europa – the petrochemical company of Eni – manages the production and marketing of Basic Chemicals, Polyethylene, Elastomers and Styrenics.

With its 17 production sites throughout Europe and a widespread sales network, Polimeri Europa can present itself to the intermediates, thermoplastic resins and elastomers market as a sound and comprehensive supplier whose key strength is its integration. From raw materials to production plants, from research laboratories to technology, through to the interface with the market which can turn to a single source with the certainty of finding solutions to its requirements not only in terms of products, but also in terms of assistance and service. Thanks to the definition of the e-commerce and the logistic portal express, Polimeri Europa can offer to its customers the opportunity to use their tailored made e-shopping and logistics. Saving time and money.

On the basis of its first hand experience, Polimeri Europa can also license its proprietary production technologies aiming to satisfy the even more specific customers needs.

Polimeri Europa's commitment to quality, improvement and innovation continues, as does its pledge to promote sustainable growth with regard to the community and the environment.

### **Licensing**

#### **Proprietary process technologies**

##### **Phenol and derivatives**

PBE-1 Zeolite catalyst based Cumene \*  
Phenol, Acetone, Alkylphenylstyrene \*  
Isopropyl Alcohol Acetone hydrogenation \*  
Isopropyl Alcohol to Cumene \*

PBE-1 Zeolite catalyst

TS-1 Titanium silicalite catalyst based  
Ammoxidation

##### **DMC and derivatives**

Dimethylcarbonate  
via Carbon Monoxide and Methanol \*  
Dimethylcarbonate / Diphenylcarbonate \*

##### **Polyethylene**

LDPE

HDPE

EVA

##### **Styrenics**

PBE-1 and PBE-2 Zeolite catalyst based

Ethylbenzene

Styrene monomer

GPPS

HIPS

EPS

ABS continuous mass polymerization

SAN

##### **Elastomers**

e-SBR

s-SBR

SBS / SB / LCBR

Polybutadiene

#### **Proprietary catalyst technologies**

Titanium silicalite

PBE-1 Zeolite

PBE-2 Zeolite

\* Co-licensing in cooperation with Lummus Technology

## **Introduction to Polimeri Europa 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. These performance properties depend in turn on the inner material properties like its rolling resistance and its heat build-up. The wide product portfolio allowed by the Polimeri Europa technology can be then used for fabrication of special tyre threads showing enhanced wet grip performance (despite of the above mentioned low rolling resistance), 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 Polimeri Europa solution SBR technology. The continuous process enables additional product grades over the ones already given by the batch process, overcoming at the same time those minor s-SBR drawbacks over e-SBR due to the narrower molecular weight distribution typically obtained in s-SBR batch process.

## **Basics of Solution SBR polymerization**

Solution polymerized styrene-butadiene rubber is obtained by anionic copolymerization of styrene and butadiene initiated by lithium alkyls in 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 absence of styrene blocks greatly improves important properties like abrasion and rolling resistances. A proper choice of modifier allows to carry out the polymerization reaction without any termination of active chain-ends; which in turn leads to high yields through the coupling or branching reactions taking place at monomers depletion. The s-SBR properties relates to both the styrene and the vinyl composition, with the latter affecting glass transition and dynamic modules, as well as to the macrostructure, which in turn affects workability. The rubber macrostructure can be efficiently managed/driven by a proper selection of 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 Polimeri Europa technology. The elastic properties of the uncured rubber are then greatly modified, allowing an easier incorporation and dispersion of the fillers.



# TECHNICAL DATA

## Material balance and process economics for typical s-SBR unit

	<i>per MT s-SBR</i>
Raw materials (Butadiene, Styrene, Aromatic Oil)	1,003 kg
Solvent make up	10 kg
Electricity – continuous	480 kWh
Electricity – batch	620 kWh
Steam (Medium pressure + Low pressure)	4,500-5,500 kg
Cooling water (Delta T +8 °C)	150-200 m <sup>3</sup>

Data are referred to 1 MT of s-SBR product, assuming 99.9 styrene and 99.7 butadiene purities.

## Expected properties

Grades	Bound styrene %	Vinyl content	Mooney viscosity ML (1+4) 100°C	Oil		Stabilizer	Main applications
				Type	p.h.r.		
<b>SOL R C2557-A</b>	25	57	54	DAE	37.5	Non staining	Silica-based compounds for low rolling resistance tyre treads with improved wet grip
<b>SOL R C2564-A</b>	25	64	50	DAE	37.5	Non staining	Silica-based compounds for low rolling resistance tyre treads with improved wet grip, mechanical good

### Industrial applications

Polimeri Europa s-SBR proprietary technology have been developed in Ravenna (Italy) R&D Center as the alternative to emulsion technology to produce new product grades and also to greatly reduce some environmental impact of the emulsion technology.

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.

### s-SBR properties

The Polimeri Europa s-SBR technology enables the production of many grades of Dry and Oil Extended polymers through batch or continuous polymerization. Changing the polymer composition (% of styrene) and polymer microstructure (% of vinyl group) is possible to obtain products 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

Polimeri Europa s-SBR grades are:

- Silica based compound for H/V tread;
- Ultra High performance tyre tread;
- Silica based compound for H/V tread winter.

Table shows an example of some product grades obtained by using Polimeri Europa s-SBR technology.



## PROCESS DESCRIPTION

Polimeri Europa s-SBR technology is based on termination-free, anionic living polymerization of styrene and butadiene, carried out in both batch or continuous process enabling production of different Dry and Oil Extended polymers. Polimeri Europa process/technology also enables production of high and medium vinyl as well as high molecular weight grades whose request comes from the highly specified tyre market. 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 (cyclohexane 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 blends 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 crumb slurry is then pumped to the finishing unit, where the crumb is dewatered on a shaker screen, being the water partly recirculated 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

Polimeri Europa 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 polymerisation carried out in continuous reactors) and feeding procedure. The competitiveness of our proprietary technology is based on the following main key-points.

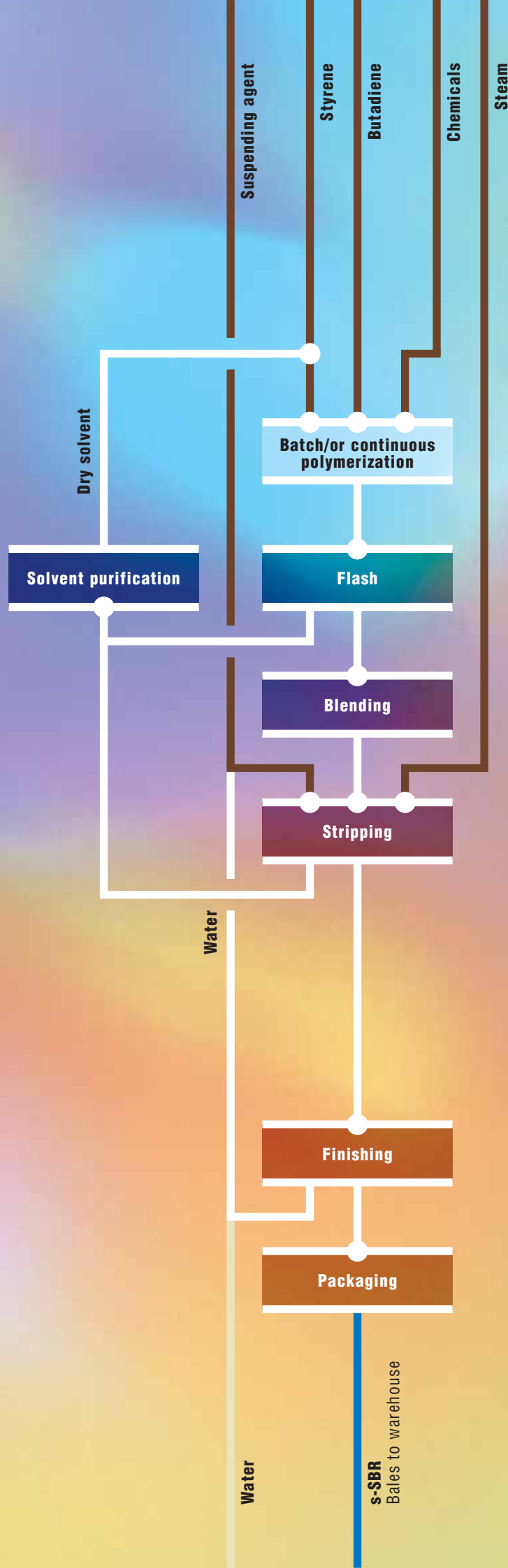
- Relevant savings in term of steam consumption due to aliphatic nature of solvent, which in turn also leads to improvements in environmental health.
- Relevant reduction in investment cost due to carrying out the reaction adiabatically, which also allows easier reaction control as well as saving in 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.
- Regular shape of crumb rubber with different density are allowed by the special design of die plate in dryer system and the proper choice of operating conditions.
- Capacity up to 60 kt/y per reaction unit are afforded, based on a single finishing line capacity up to 30 kt/y.
- 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.

Raw materials

Process sections

Products

By products



## Polimeri Europa SpA

A subsidiary of Eni SpA  
Sole shareholder company

### Head Office

Piazza Boldrini, 1  
20097 San Donato Milanese (Milano) – Italy  
t +39 02 520.1  
info@polimerieuropa.com  
www.polimerieuropa.com

### Licensing

Piazza Boldrini, 1  
20097 San Donato Milanese (Milano) – Italy  
t +39 02 520.32883  
f +39 02 520.32077  
info.licensing@polimerieuropa.com



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