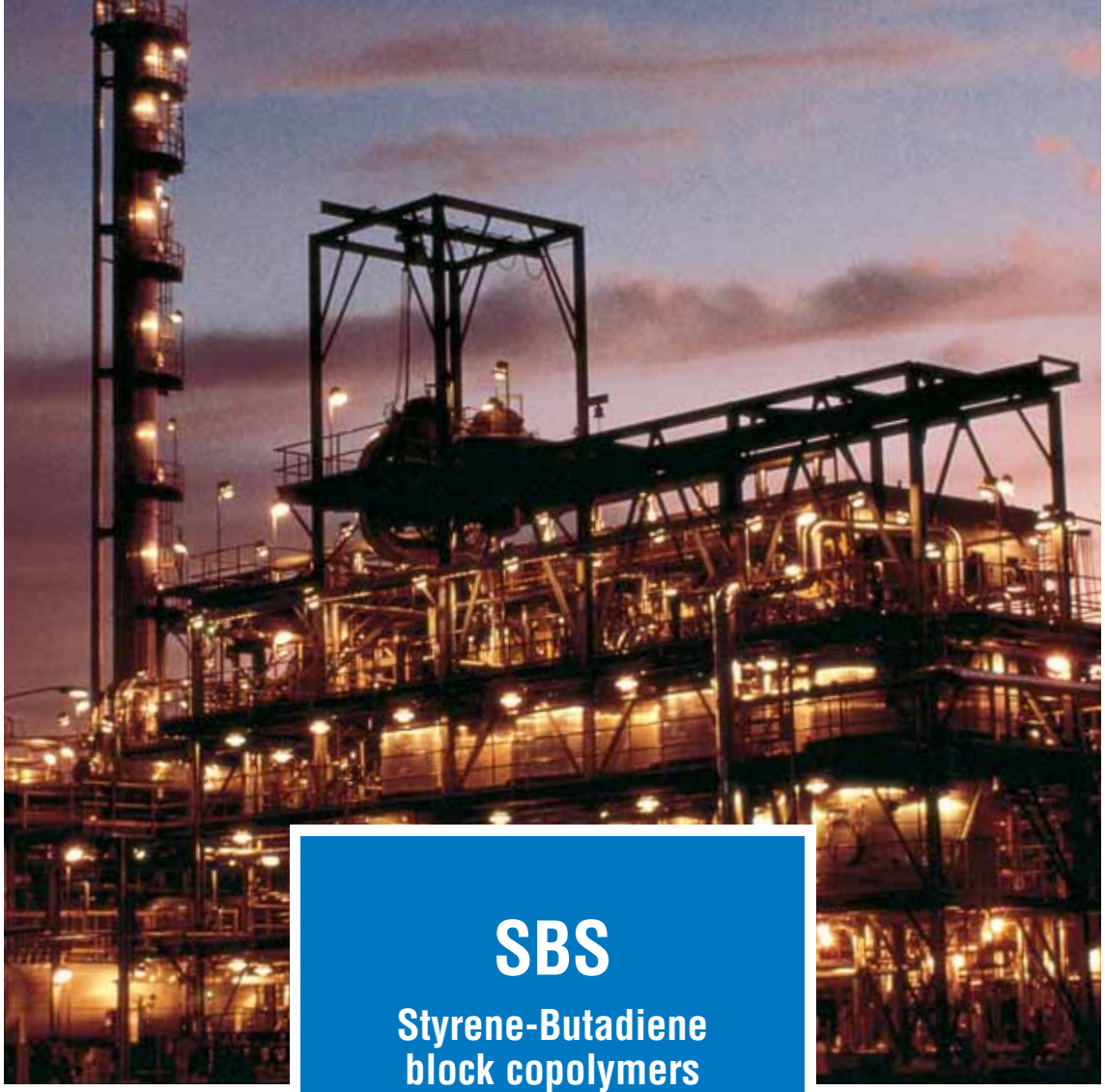


SBS

Styrene-Butadiene block copolymers

Proprietary process technology

eni

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, Alphamethylstyrene *
Isopropyl Alcohol Acetone hydrogenation *
Isopropyl Alcohol to Cumene *
PBE-1 Zeolite catalyst
TS-1 Titanium silicalite catalyst based
Ammoximation

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 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.

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.

Polimeri Europa 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.

Polimeri Europa SBS technology allows then competitive production of the most common SBS grades, as well as additional grades for special applications.

Such portfolio of products is continuously improved by our R&D centers through market feedback.

TECHNICAL DATA

Material balance and process economics

Per MT of Oil Extended SBS	
Butadiene + Styrene + Paraffinic oil extensor	1,003 kg
Solvent make up	10 kg
Electricity	510 kWh
Steam (medium pressure + low pressure [1])	4,500 kg
Cooling water (delta T + 8 °C)	200 m^3
Per MT of Dry SBS	
Butadiene + Styrene	1,001 kg
Solvent make up	10 kg
Electricity	510 kWh
Steam (medium pressure + low pressure [1])	5,000 kg
Cooling water (delta T + 8 °C)	200 m^3

[1] 10 barg and 6 barg respectively.

Industrial applications

Polimeri Europa is currently one of the major industrial producer of SBS polymer. Two industrial units worldwide, in Italy and US, are currently based on proprietary SBS technology.
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 Polimeri Europa.

Expected properties

Oil Extended Types

Grades	Block styrene % ASTM D5775	Oil % w/w ASTM D5774	Structure	Mw/1000 MA 02225 [1]	Diblock content % MA 02225 [1]	Melt flow index [2] ASTM 1238	Hardness [3] Shore A ASTM D2240	Physical form [4]	Main applications
Europrene® SOL T 172	30	31	Radial	165	<10	9	43	PL	Footwear, polymer modification and plastic recycling, technical goods
Europrene® SOL T 177	50	28,5	Radial	145	<10	15	86	PL	Footwear, high hardness sheets and soles

Dry Types

Grades	Block styrene % ASTM D5775	Diblock content % MA 02225 [1]	Structure	Mw/1000 MA 02225 [1]	Brookfield viscosity cPs [5]	Melt flow index [2] ASTM 1238	Hardness [3] Shore A ASTM D2240	Physical form [4]	Main applications
Europrene® SOL T 161 B	30	10	Radial	240	20,000	<1	82	G, P	Bitumen modification for roofing and road paving
Europrene® SOL T 166	30	10	Linear	70	1,300	6	72	PL	Moulded and extruded goods, polymer modification, adhesives
Europrene® SOL T 6302	30	12	Linear	110	4,000	<1	80	G, F, P	Bitumen modification for roofing and road paving, compounding

[1] Internal method.
[2] Modified P conditions (5 kg, 190 °C).
[3] Values obtained on compression moulded specimen.
[4] PL = pellets; G = granules; F = fluffy granule; P = powder.
[5] Toluene solution, 25% by weight.

Basics of SBS polymerization

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 triblock 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 one polymerization process as well as from the two stages, 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 polibutadiene 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.

The Europrene® SBS block copolymer properties and 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 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.

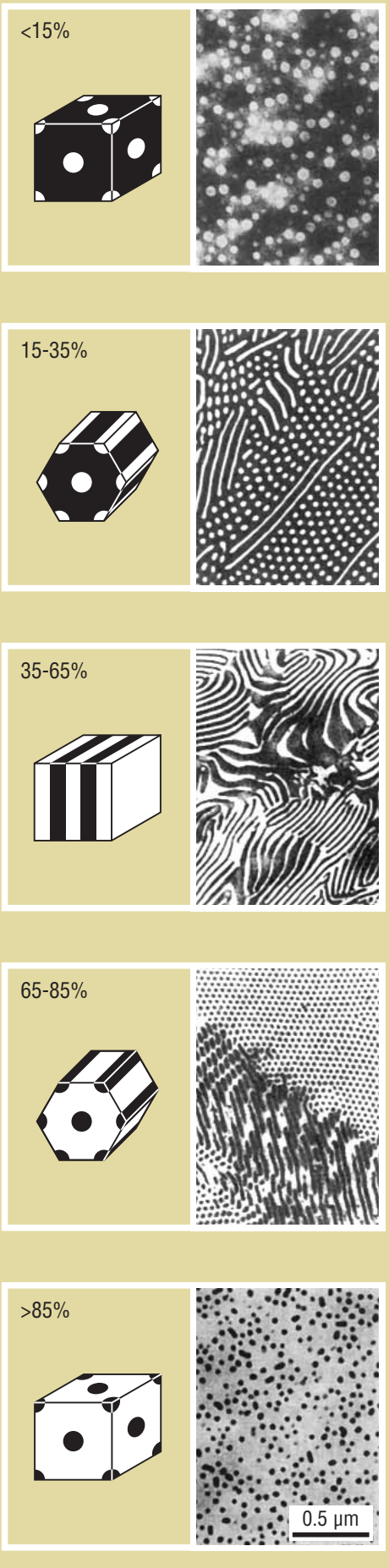
A proper pre-definition of both molecular weights and molecular weight distribution of the blocks, as well as their purity, avoids the progressive worsening of the mechanical characteristics due to poor phase separation. Prevention of unwanted broadening of molecular weight distributions is guaranteed by using highly purified and dried monomers preventing uncontrolled termination of "living" chain-ends.

The Polimeri Europa 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.

The following tables give to our potential customers a picture of different typical properties and applications for some Dry and Oil Extended product grades affordable by using Polimeri Europa proprietary SBS technology.

All polymer grades are stabilized with a specifically designed antioxidant package.

Amount of Styrene in S-B-Blockcopolymers

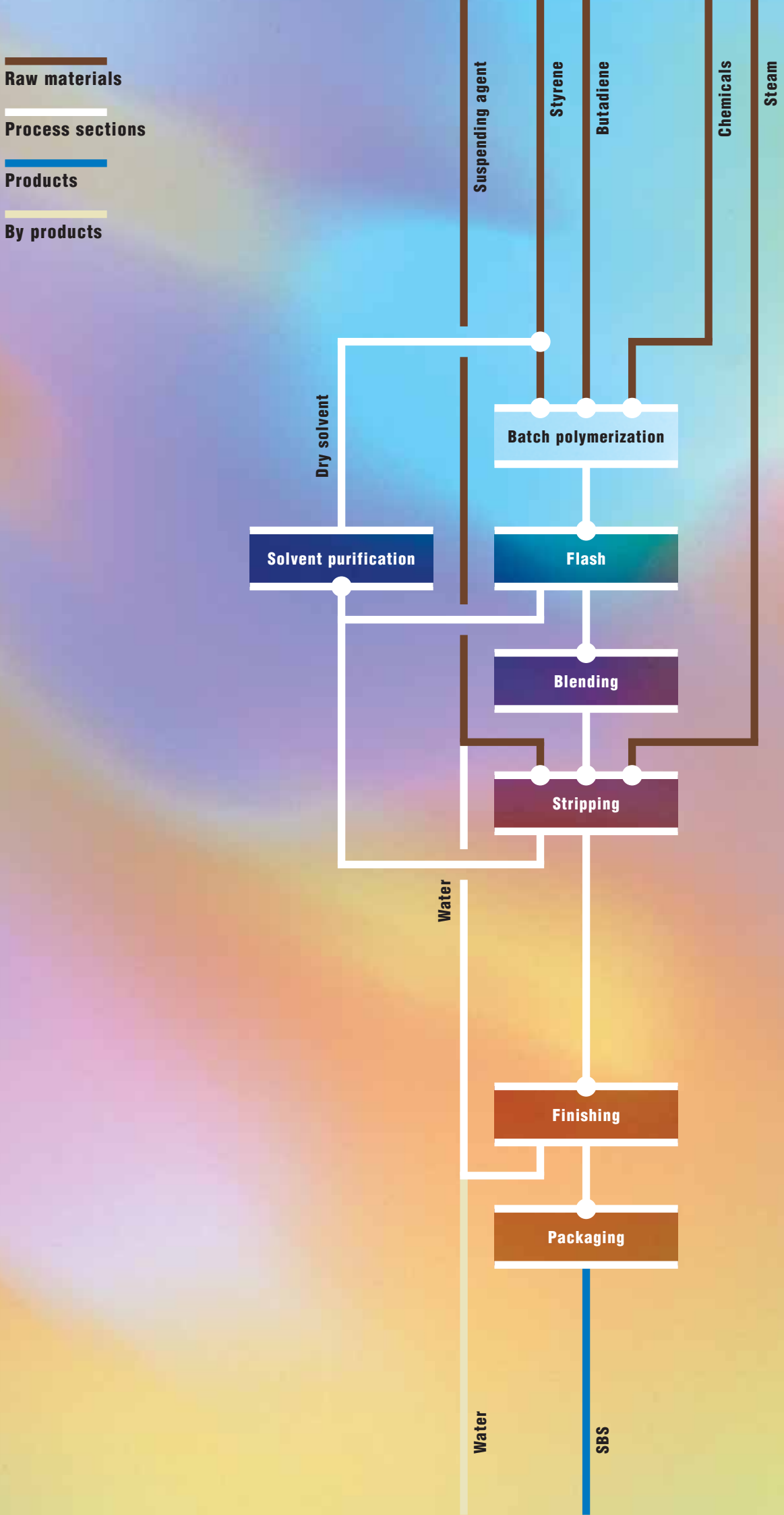


PROCESS DESCRIPTION

The Polimeri Europa SBS technology is based on a sequential process through a “living” anionic polymerization reaction of styrene and butadiene leading to polymer structures composed of styrene blocks at each end (hard phase), connected by polybutadiene blocks (soft phase).
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 (50 m^3).
  Capacity up to 50 kt/y for single reaction line is then afforded by using three batch reactors, lowering the investment cost.
  Capacity up to 30 kt/y per single finishing line is available.
- Technology does not have proprietary items.
- 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.


Raw materials
Process sections
Products
By products
Suspending agent
Styrene
Butadiene
Chemicals
Steam
Dry solvent
Batch polymerization
Solvent purification
Flash
Blending
Stripping
Water
Finishing
Packaging
Water
SBS

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Responsible Care

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