ELASTOMERS

Impact improvement

HIPS/ABS

APPLICATION

versalis

Impact improvement of HIPS/ABS

INTRODUCTION

Materials in the Versalis elastomers portfolio are well suited to the impact modification of polystyrene. These impact-modified polystyrenes, namely high impact polystyrene (HIPS) and acrylonitrile-butadiene-styrene (ABS) possess superior shock-resistant properties over general purpose polystyrene (GPPS).
The Versalis elastomers used in the preparation of HIPS and ABS are low-cis BR (Intene®) and S-SBR (Europrene SOL B). The dry-blending of SOL B or SOL T with HIPS or GPPS also allows for additional types of modified polystyrenes to be prepared.

Low-Cis BR (Intene®)

BACKGROUND

Low-cis polybutadiene rubber (BR) produced by a solution process was developed in the 1950-60's and arose from the increasing interest in the use of anionic polymerisation to create polybutadienes of consistent and precise structure. The Versalis site at Grangemouth (UK) commenced production of low-cis BR in the early 1960's, primarily for the tyre industry, but such products soon began to find uses in the modification of plastics.
Over time, low-cis BR (both linear and branched) has become the product of choice for the industrial modification of plastics in High Impact Polystyrene (HIPS) or Acrylonitrile-Butadiene-Styrene (ABS).
The trade name for Versalis low-cis BR is Intene®.

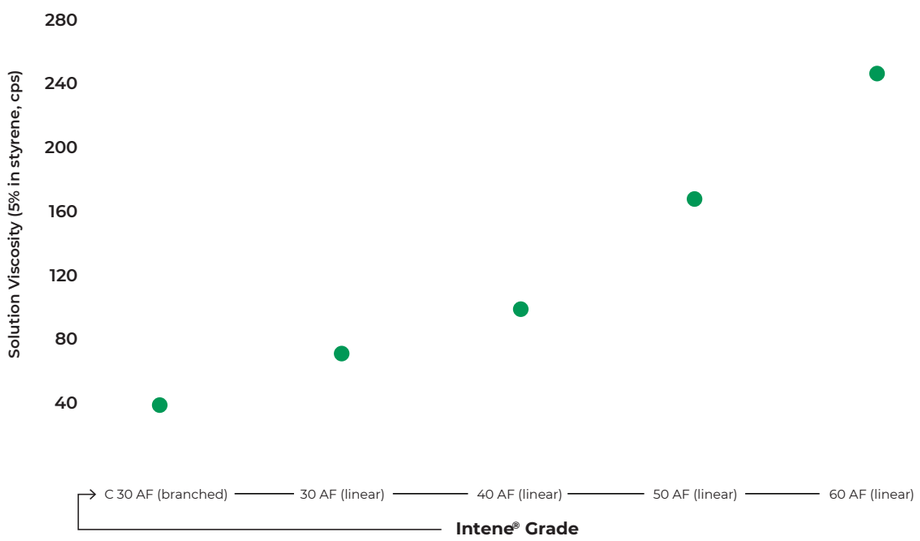
PROCESS

Solution polymerised low-cis butadiene rubber is obtained by the continuous anionic living polymerisation of butadiene initiated by lithium alkyls in hydrocarbon solvent. The finishing process consists of solvent stripping and stabilisation, the latter by the addition of an appropriate non-staining antioxidant. The final stage is one in which the polymer crumb is dried, baled and packaged.

MAIN PROPERTIES

The main criteria of low-cis BR for plastics modification are low gel and colour, low dissolution time in styrene and well-characterised solution viscosity. Solution viscosity in styrene dictates the final properties of the modified plastic and, as such, is the principal selection parameter for the customer. The graph below (fig. 1) shows solution viscosity of linear and branched Intene® available from Versalis.

Fig. 1



LOW-CIS BR PORTFOLIO

Versalis provides a wide range of low-cis BR grades to suit all HIPS/ABS manufacturers requirements as shown below:

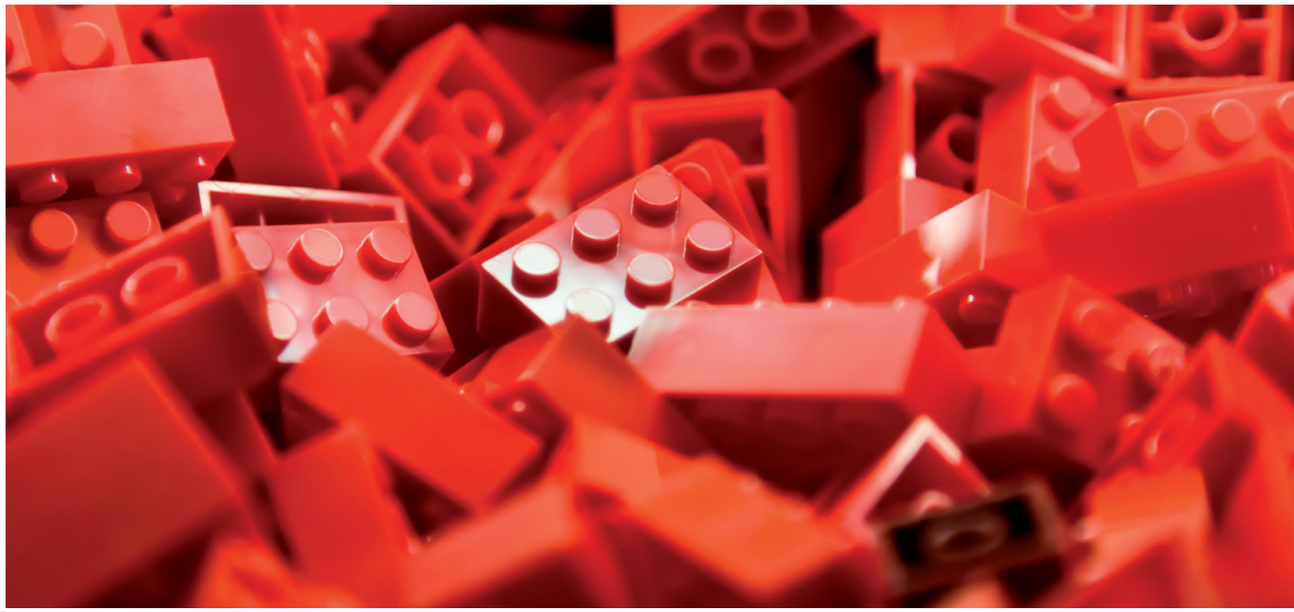
GRADE	ANTIOXIDANT	POLYMERISATION PROCESS (STRUCTURE)	SOLUTION VISCOSITY (CPS)	COLOUR (B*) (MAX)	APPLICATION
Intene® C 30 AF	BHT/TNPP-free	Continuous (branched)	30-50	5	HIPS (high gloss) / ABS
Intene® 30 AF	BHT/TNPP-free	Continuous (linear)	55-75	5	HIPS (high gloss) / ABS
Intene® 40 AF	BHT/TNPP-free	Continuous (linear)	80-120	5	HIPS (medium gloss) / ABS
Intene® 50 AF	BHT/TNPP-free	Continuous (linear)	150-190	5	HIPS
Intene® 60 AF	BHT/TNPP-free	Continuous (linear)	230-270	5	HIPS (super impact / ESCR)

STORAGE AND PACKAGING

The Intene® grades should be stored in the containers provided within a vented dry enclosed area at temperatures between 20-30°C away from direct sunlight. The shelf life of Intene® grades is 12 months minimum. All grades are in the form of bales and the packaging and contents details are given below:

GRADE	PACKAGING	DIMENSIONS (mm)	NOMINAL WEIGHT (kg)	PHYSICAL FORM	BALE WEIGHT (kg)	BALES TOTAL	BALES X LAYER	FILM TYPE
Intene® 40 AF	metal crate	1465x1150x1123	1,188	bales	33	36	6x6	PS
Intene® 50 AF	metal crate	1465x1150x1123	1,188	bales	33	36	6x6	PS
Intene® 60 AF	metal crate	1465x1150x1123	1,188	bales	33	36	6x6	PS
Intene® C 30 AF	metal crate	1465x1150x1123	900	bales	30	30	6x5	PS
Intene® 30 AF	metal crate	1465x1150x1123	1,188	bales	33	33	6x6	PS

S-SBR (Europrene® SOL B)



BACKGROUND

Versalis offers both random “R” and block “B” solution styrene-butadiene elastomers in its portfolio, but it is the “B” type which is be used in the preparation of HIPS or ABS. The historical development of SOL B type polymers (SB di-blocks) arrived somewhat later than that of low-cis polybutadiene rubber and the Versalis site at Grangemouth (UK) commenced production of SOL B in the early 1990’s.

PROCESS

SOL B rubber is obtained by anionic living polymerisation of butadiene and styrene initiated by lithium alkyls in hydrocarbon solvent. The finishing process consists of solvent stripping and stabilisation, the latter by the addition of an appropriate non-staining antioxidant. The final stage is one in which the polymer crumb is dried, baled and packaged.

MAIN PROPERTIES

SOL B elastomers can be used alone or in combination with Intene® for HIPS or ABS depending on the property requirements of the final material and can provide a glossiness or transparency to the final product. Typically the Intene® used for such an application has low solution viscosity, i.e., Intene® C 30 AF, Intene® 30 AF or Intene® 40 AF. The main properties of the final material are Izod impact strength and gloss and the table below shows how the proportion of Intene® and SOL B affect these key properties:

INTENE® + SOL B	HIPS IZOD IMPACT STRENGTH	GLOSS
Intene® % > SOL B %	↑	↓
Intene® % ~ = SOL B %	↑	↑
Intene® % < SOL B %	↓	↑

SOL B portfolio

GRADE	ANTIOXIDANT	BOUND STYRENE WT%	BLOCK STYRENE WT%	VISCOSITY 5% IN STYRENE (CPS)	APPLICATION
Europrene® SOL B 1205	BHT / TNPP-free	26	50	-	Medium glossy HIPS
Europrene® SOL X C283	BHT / TNPP-free	11	8	35	Impact improver of ABS and Polystyrene giving a gloss surface

STORAGE AND PACKAGING

The SOL B grades should be stored in the containers provided within a vented dry enclosed area at temperatures between 20-30°C away from direct sunlight. The shelf life of SOL B grades is 12 months minimum. All grades are in the form of bales and the packaging and contents details are given below:

GRADE	PACKAGING	DIMENSIONS (mm)	NOMINAL WEIGHT (kg)	PHYSICAL FORM	BALE WEIGHT (kg)	BALES TOTAL	BALES X LAYER	FILM TYPE
Europrene® SOL B 1205	metal crate	1465x1150x1123	990	Bales	33	30	6x5	PE
Europrene® SOL X C283	metal crate	1465x1150x1123	1080	Bales	30	36	6x6	PS

Application PS/ABS
Solution process

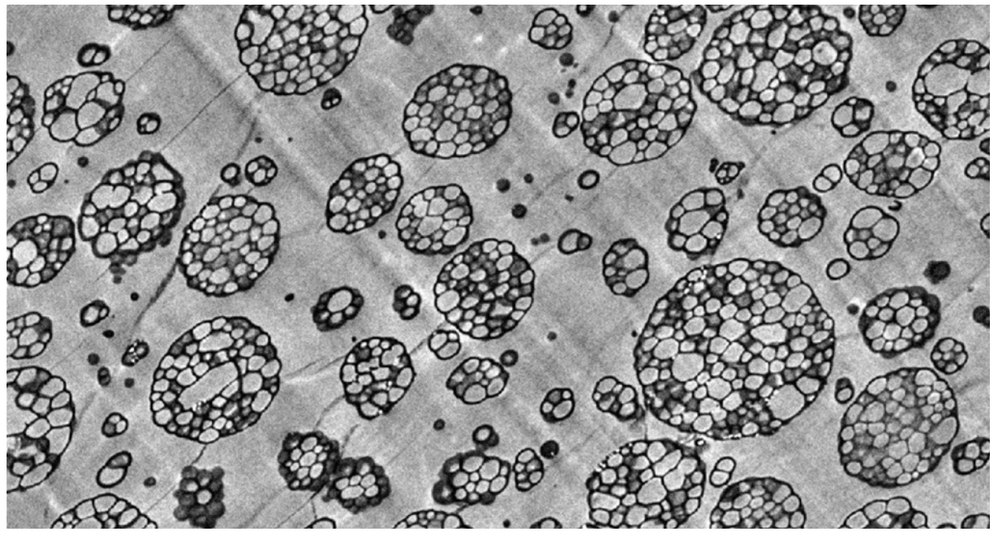
HIGH IMPACT POLYSTYRENE (HIPS)

Polystyrene is a plastic material with high tensile strength, but it is brittle. The incorporation of a rubber (e.g. Intene®) at 5-10% allows the polystyrene to absorb energy and inhibits crack growth preventing fracture and brittleness.

HIPS is produced by the polymerisation of styrene in the presence of the rubber by means of an organic peroxide initiator and undergoes a number of phases which are critical to the properties of the final product.
Initally, before the necessary phase inversion process takes place, the material is a dispersion of polystyrene droplets in rubber solution with the rubber forming the continuous phase (~5% conversion). As polymerisation progresses (10-12%), polystyrene becomes the continous phase and a multiple emulsion forms where rubber partices contain sub-inclusions of polystyrene; this is the critical phase inversion step.
After phase inversion the form of the final product is one of a dispersion of rubber in polystyrene.

Such a matrix of polystyrene with rubber occlusions, morphology, is demonstrated clearly in fig. 2.

Fig. 2 Transmission Electrom Microscopy of HIPS morphology



As stated briefly above, the mechanism by which HIPS reinforcement occurs is one of prevention of crack growth; the rubber occlusions act as “energy-sinks” when the material is subject to stress. Cracks in the material are prevent from reaching a critical level.

The required balance of properties of HIPS is influenced greatly by the molecular weight and structure of the Intene® used - examples of such properties would be flow, heat distortion temperature, tensile modulus, impact strength and gloss. Two of the main properties are Izod impact strength and gloss. The table below shows how, in very broad terms, the molecular weight and structure of the Intene® grades affect these key properties:

GRADE	LINEAR OR BRANCHED	MOLECULAR WEIGHT	HIPS IZOD IMPACT STRENGTH	HIPS GLOSS
Intene® 60 AF	Linear	↑	↑	↓
Intene® 50 AF	Linear		↑	↓
Intene® 40 AF	Linear		↓	↑
Intene® 30 AF	Linear		↓	↑
Intene® C 30 AF	Branched		↓	↑

Application PS/ABS
Solution process

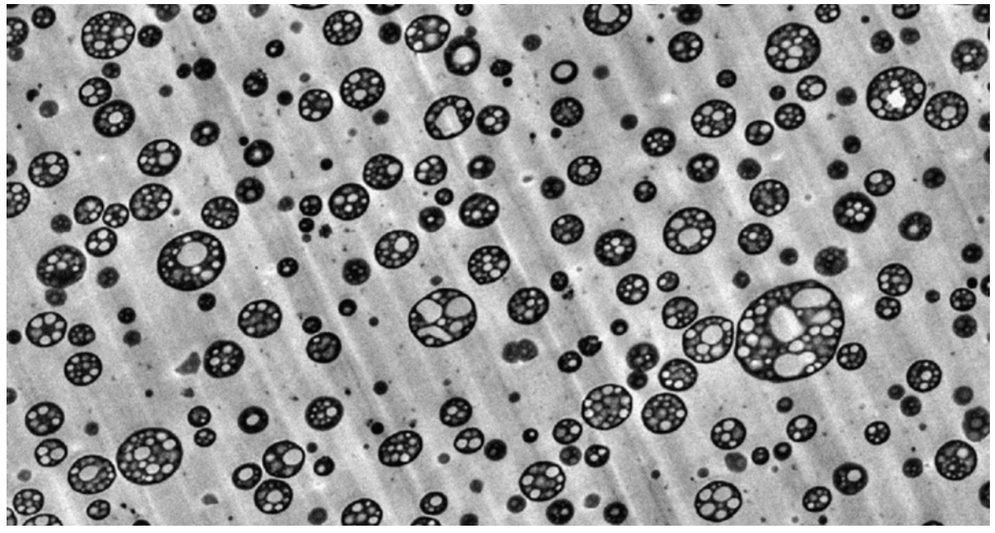
HIGH GLOSS HIPS

High gloss HIPS is of interest to many manufacturers and Intene® C 30 AF or Intene® 30 AF is useful for this purpose. The very low solution viscosity of Intene® C 30 AF or Intene® 30 AF produces small rubber occlusions in the HIPS and this provides for a higher gloss finish. In high gloss HIPS, Intene® C 30 AF or Intene® 30 AF is typically used in together with an SB di-block copolymer (Europrene SOL B) to give the correct balance of gloss and Izod impact.
Intene® 40 AF also has a low solution viscosity and can be used for some medium gloss applications.

ACRYLONITRILE-BUTADIENE-STYRENE (ABS)

The process of manufacture of ABS is similar to that of HIPS but in this case the rubber is dissolved in acrylonitrile/styrene instead of styrene. The effects of the type of rubber used on the properties of ABS are also similar to HIPS. For optimum results the rubber particle size in ABS is very important and for this reason an Intene® polymer with low solution viscosity such as Intene® C 30 AF is favoured, although Intene® 40 AF can be used in some manufacturers processes.
An example of ABS morphology is shown below (fig. 3) and it can be noted that the rubber particles are smaller in general than the HIPS counterpart.

Fig. 3 Mass-continuous ABS morphology



SBC Europrene SOL T

BACKGROUND

The TPR plant, located in Ravenna, Italy, is on stream since 1971. Versalis is manufacturing styrenic block copolymers commercialized under the trade names: Europrene® SOL T (SBS, SBC and SIS) and Europrene® SOL TH (SEBS).

PROCESS

SBC are obtained by an anionic polymerization initiated by lithium alkyls in aliphatic solvent. Flexibility is the main feature of this polymerization technique that enables the production of thermoplastic elastomers differentiated by chemical composition, molecular weight and molecular architecture, allowing linear and star copolymers.

MAIN PROPERTIES

Dry blending is greatly facilitated by free flowing physical forms. Styrene-Butadiene Block Copolymers in fact can be fed in an extruder with GPPS and/or GPPS/HIPS mix to improve their impact resistance. The grades of choice are typically dry grades characterized by medium/medium-high styrene content (30-40%) and medium molecular weight (MFI 190°C, 5 kg > 5 g/10').

TPR (Europrene® SOL T) portfolio

GRADE	ANTIOXIDANT	STRUCTURE	BOUND STYRENE WT%	DI-BLOCK WT%	APPLICATION
Europrene® SOL T 166	BHT/TNPP-free	linear	30	10	Moulded and extruded goods, polymer modification, adhesive
Europrene® SOL T 6320	BHT/TNPP-free	linear	31	75	Bitumen modification, polymer modification, adhesives
Europrene® SOL T 6414	BHT/TNPP-free	radial	40	22	Compounding, polymer modification, adhesives

Application GPPS/HIPS Dry-blending

MODIFICATION OF GPPS AND HIPS VIA DRY-BLENDIN

HIPS and GPPS can be modified by dry-blending with SOL B or SOL T SBC and this type of manufacture can provide a convenient alternative to the more complex solution/grafting processes.

Europrene® SOL T is particularly suitable for this process and the wide choice of available grades by Versalis, differing in molecular weight and composition, allow an informed choice to be made depending on the final properties required.

Typical examples of polystyrene modification with SOL T products are:
- toughening of GPPS;
- upgrading of recycled GPPS/HIPS;
- HIPS-based reinforcing flame-retardant additives.

SOL T materials specifically designed for plastics modification by dry-blending are:
- SOL T 166;
- SOL T 6320;
- SOL T 6414.

The example beside shows clearly the effect of 3- 15% SOL T 166 to either GPPS or HIPS; significant improvement is seen in the IZOD impact strength, elongation and low temperature behaviour.

Composition: GPPS + SOL T

GPPS (%)	100	95	90	85
Europrene® SOL T 166 (%)	-	5	10	15

Properties

MFR @ 200°C, 5 kg (g/10²)	5.5	6.5	7.5	8.5
Flexural Modulus (MPa)	3000	2800	2610	2380
Yeld Stress (MPa)	-	42	40	33
Stress at Breack (MPa)	48	33	29	27
Elongation at Breack (%)	-	18	35	40
Notched Izod Impact Strength @ R.T. (J/m)	15	16	20	25

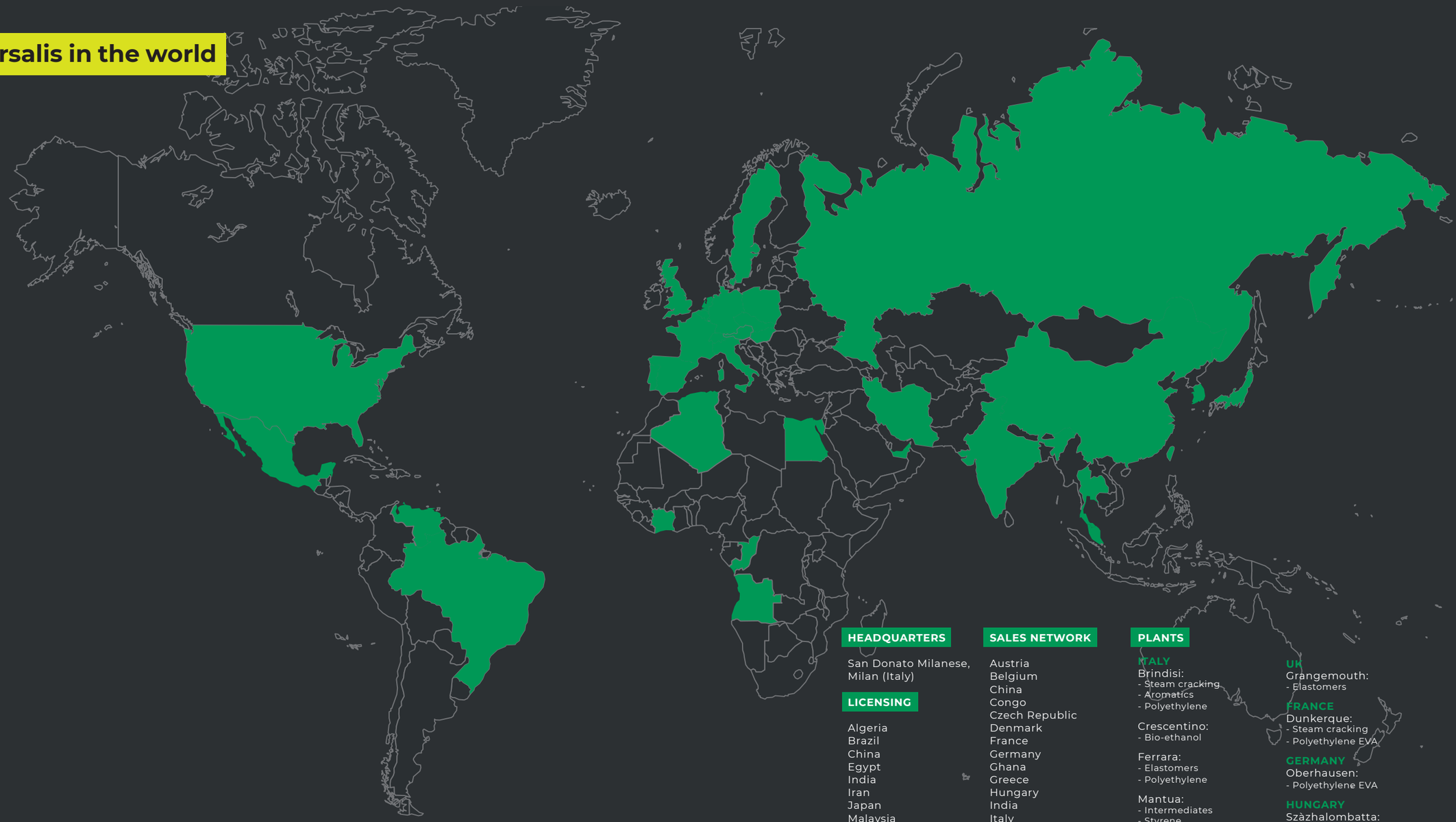
Composition: HIPS + SOL T

HIPS (%)	100	95	90	85
Europrene® SOL T 166 (%)	-	5	10	15

Properties

MFR @ 200°C, 5 kg (g/10²)	5	5	5	6
Flexural Modulus (MPa)	1790	1680	1600	1310
Yeld Stress (MPa)	23	22	22	19
Stress at Breack (MPa)	24	23	23	20
Elongation at Breack (%)	48	48	57	68
Notched Izod Impact Strength @ R.T. (J/m)	100	110	120	165
Notched Izod Impact Strength @ -20°C (J/m)	70	90	100	120

Versalis in the world



Versalis is focused on establishing itself as a solution provider, offering a range of increasingly market-oriented products at an international level. The company is present in the APAC region through its Shanghai-based subsidiary, Versalis Pacific Trading; in Mumbai, India; in Singapore; and in South Korea through LVE, a joint venture with Lotte Chemical.

Versalis can also count on subsidiaries Versalis Americas – with offices in Houston, Texas – and Versalis Mexico. Furthermore, Versalis serves the oil and gas industry with offices in Ghana and in Congo, with its portfolio of oilfield chemicals. Thanks to a widespread sales network, distributors and sales agents, Versalis can serve all markets worldwide.

HEADQUARTERS

San Donato Milanese, Milan (Italy)

LICENSING

Algeria
Brazil
China
Egypt
India
Iran
Japan
Malaysia
Portugal
Qatar
Romania
Russian Federation
Slovak Republic
South Korea
Spain
Taiwan
USA
Venezuela

R&D

ITALY
Ferrara
Mantua
Novara
Porto Torres
Ravenna
Rivalta Scrivia

SALES NETWORK

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China
Congo
Czech Republic
Denmark
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Greece
Hungary
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Mexico
Poland
Portugal
Romania
Russian Federation
Singapore
Slovak Republic
South Korea
Spain
Switzerland
Sweden
Turkey
United Arab Emirates (VPM, a joint venture with Petrochem/Mazrui Energy Services)
UK
USA

PLANTS

ITALY
Brindisi:
- Steam cracking
- Aromatics
- Polyethylene

Crescentino:
- Bio-ethanol

Ferrara:
- Elastomers
- Polyethylene

Mantua:
- Intermediates
- Styrene
- Styrenics

Porto Marghera:
- Recycled polymers

Porto Torres:
- Elastomers
- Renewable chemistry

Priolo:
- Steam cracking
- Aromatics

Ragusa:
- Polyethylene EVA
- Butadiene

Ravenna:
- Elastomers

UK
Grangemouth:
- Elastomers

FRANCE
Dunkerque:
- Steam cracking
- Polyethylene EVA

GERMANY
Oberhausen:
- Polyethylene EVA

HUNGARY
Szàzhalombatta:
- Styrenics

SOUTH KOREA
Yeosu (LVE, a joint venture with Lotte Chemical):
- Elastomers

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