SIPOL

SOCIETÀ ITALIANA POLIMERI

SIPOLPRENE®

ETHER ESTER THERMOPLASTIC ELASTOMERS

GENERAL INFORMATION

SIPOLPRENE® is the registered trade mark of SIPOL S.p.A. for its family of thermoplastic ether-ester elastomers. These engineering polymers are made through the combination of rigid polyester blocks (crystalline segment) and flexible long-chain polyether blocks (amorphous segment). By varying the structure of these blocks it is possible to determine the final properties of the polymers.

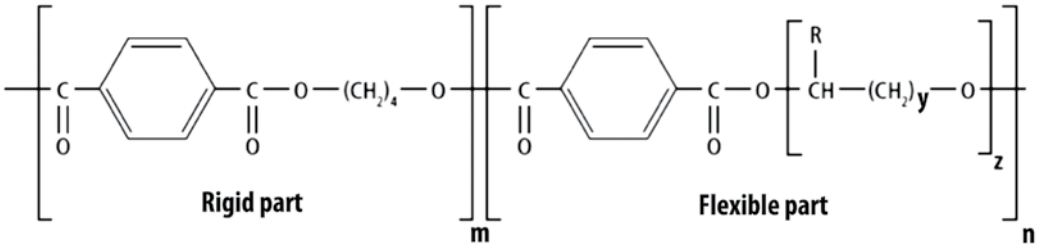

FIG. 1. SIPOLPRENE® molecular structure

The rigid part is basically a PBT chain, while the flexible part is a polyether. The higher the number **n**, the softer is the resulting polymer. In the opposite sense, by bringing ideally **n** to 0 the polymer becomes a simple PBT. It is evident that the ratio between rigid and flexible segments is the first and simplest way to drive the polymer hardness.
A second level of modification can be achieved by tuning parameter **z**, the molecular weight of the polyether chain. This, of course, modifies the polymer characteristics as concerns mechanical properties vs temperature, gas permeability, and chemical resistance. Additional modifications can be achieved by changing **R** and **y** (the ether unit), thus modifying the polymer polarity.

The double soul of the SIPOLPRENE® macro molecular chain (polyester – rigid and polyether – soft) allows the polymer to match the qualities of flexible plastics with the performance of thermoset elastomers. As thermoplastic elastomer, it can easily be processed by using many different techniques, such as injection molding, extrusion, blow molding, etc.
At microscopic levels, the resulting structure, which is a block copolymer made of short hard segments alternating with long flexible segments, is biphasic in morphology. The presence of hard polyester blocks assures heat resistance, chemical resistance and easy processing; amorphous polyether regions improve softness and elasticity, directly connected to the material hardness.

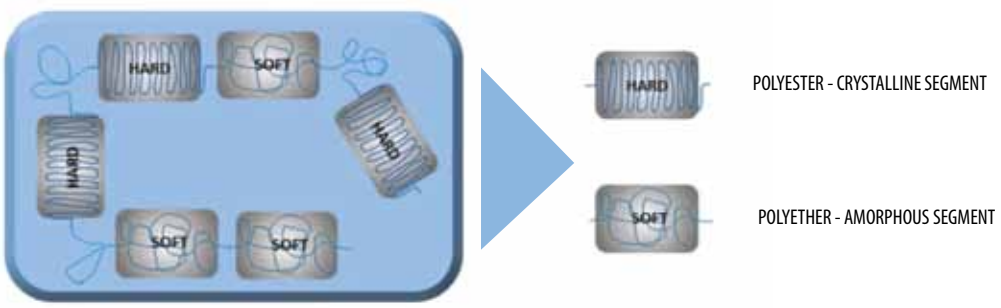

FIG. 2. SIPOLPRENE® microstructure

One of the most important characteristics that makes SIPOLPRENE® different from most engineering plastic resins and thermoplastic elastomers is that all SIPOLPRENE® products show mechanical characteristics due to their block copolymer structure (modulus, tenacity and resilience) less affected by temperature variations. This higher mechanical performance constancy makes SIPOLPRENE® the right engineering choice for applications where a high standard is required for safety or reliability reasons.

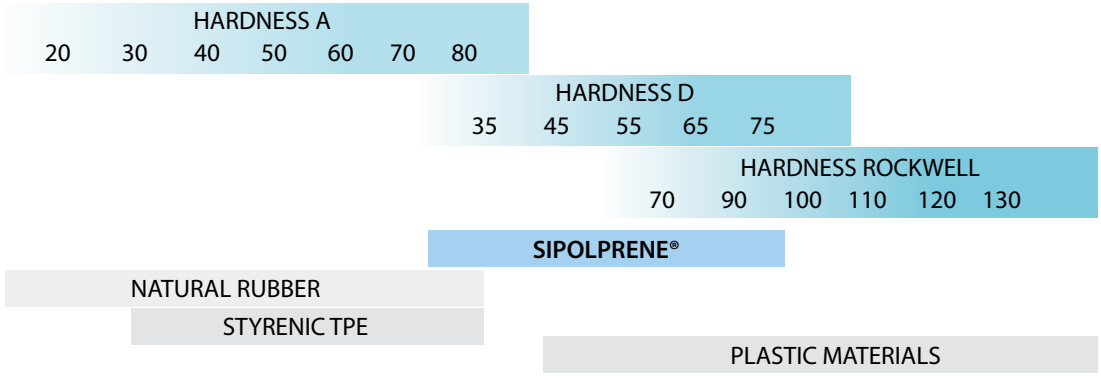

FIG. 3. SIPOLPRENE® compared to other plastics and rubber according to different hardness scales

PRODUCT RANGE AND PRODUCT CODING

SIPOLPRENE® range consists of High Performance and Specialty grades of various melting points and hardness levels.

Main Code is composed of five digits XXYYY where the first two roughly indicate the hardness ShD (XX) and the remaining three (YYY) indicate melting temperature.

TYPE	HARDNESS SHORE D (instantaneous)	MELTING TEMPERATURE (°C)
HIGH PERFORMANCE GRADES		
SIPOLPRENE® 25170	27	173
SIPOLPRENE® 25185	29	184
SIPOLPRENE® 35180	35	177
SIPOLPRENE® 35195	35	195
SIPOLPRENE® 46185	44	186
SIPOLPRENE® 55200	52	198
SIPOLPRENE® 58210	58	211
SIPOLPRENE® 63210	63	211
SIPOLPRENE® 72220	72	219

Fig. 4. SIPOLPRENE® High Performance grades

In addition to the above High Performance grades, Sipol has been developing special products, targeting specific applications or specific performance:

- SIPOLPRENE® 35150, where melting temperature is lowered to 150 °C so as to make it suitable for PVC modification by compounding (polymer alloy).
- SIPOLPRENE® reporting "1" as last digit (SIPOLPRENE® 55211 and SIPOLPRENE® 40171) is modified so as to increase crystallization rate, offering faster cycles in injection molding.

A *Secondary Code* can be added for non-standard viscosity, specific stabilization package and black versions.

CODE	DESCRIPTION
LV	Low viscosity
HV	High viscosity directly achieved in polymerization
R	Very high viscosity reached through solid state polymerization
K	Heat stabilized through masterbatch dry blending
W	UV stabilized through masterbatch dry blending
MD	Metal de-activated for high performance cable jacketing
N	Improved NOx resistance
H	Hydrolysis stabilized through masterbatch dry blending
B	Black coloring through masterbatch dry blending

Fig. 5. SIPOLPRENE® product coding: additives and coloring

PHYSICAL - MECHANICAL PROPERTIES

SIPOLPRENE® materials combine flexibility, temperature and chemical resistance with dimensional stability, flexural fatigue resistance and high impact strength. SIPOLPRENE® products have a good abrasion and tear resistance, good electrical properties and an excellent overmolding adhesion to various plastic materials due to their polar structure.

Mechanical properties of various SIPOLPRENE® products are strictly related to both their chemical composition and hardness. The more the hard-block content (rigid polyester), the more the hardness and they pass from essentially elastomeric polymers (27–44 Shore D) to plastomeric ones (52–72 Shore D). The result is an increasing load, stiffness, tear, creep, chemical and temperature resistance. Equally there is a decrease in fatigue and impact resistance.

Their field of application covers a wide temperature range, starting from -65 °C up to 185 °C, depending on the grade selected.

low / medium / high	SOFT GRADES 27-44 Sh D	HARD GRADES 52-72 Sh D
Hard segment content	■	■
Soft segment content	■	■
Crystallinity	■	■
Flexibility	■	■
Dimensional stability	■	■
Creep resistance	■	■
Thermal stability	■ ■	■
Chemical resistance	■	■
Low-temperature impact	■	■
Flex fatigue	■	■

Fig. 6. SIPOLPRENE® characteristics

The best way to comprehend the elastic behaviour of SIPOLPRENE® is to refer to their stress/strain curves. Tensile strength values are obtained from stress/strain curves determining the point of maximum stress on the curve. Maximum tensile values can be used in rating the relative material strain strength: generally the softer the polymer the lower the yield point and the higher the elongation at yield. This defines the strain range where the material has elastic properties.

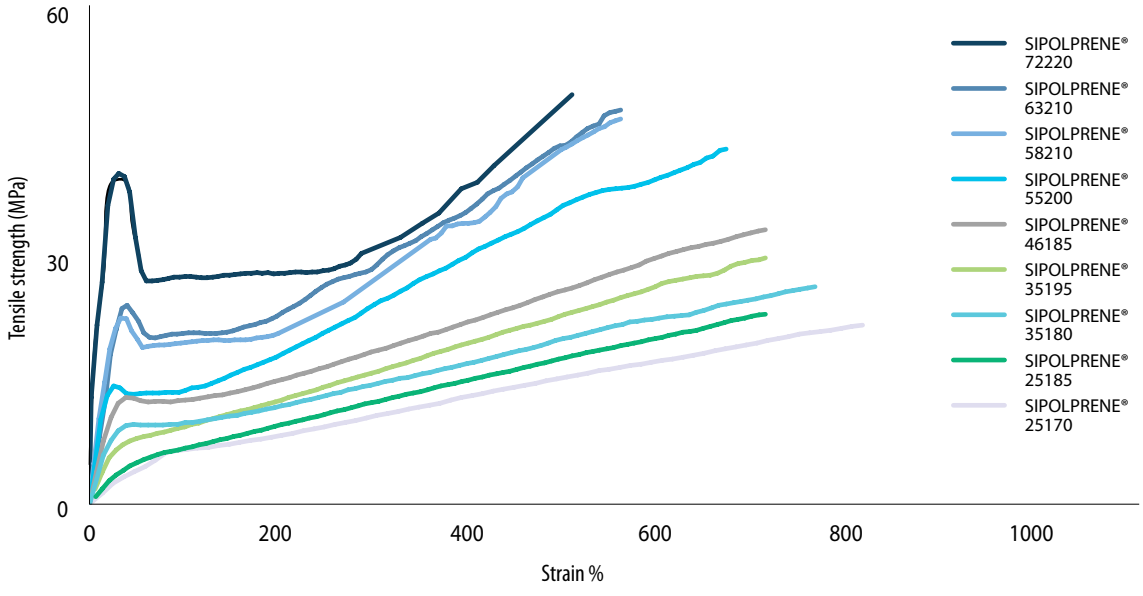

FIG. 7. SIPOLPRENE® stress/strain curves, registered at 25 °C

SIPOLPRENE®'s outstanding creep resistance is explained by its excellent retention of mechanical properties under constant load, for long periods of time. This important feature makes it the ideal candidate for automotive, sealing and snap fit applications. SIPOLPRENE®'s high resistance to creep ensures that parts will be long lasting. Finally, SIPOLPRENE® has excellent compression set resistance compared to other thermoplastic elastomers.

RESISTANCE TO CHEMICALS AND OILS

Having a polyester skeleton SIPOLPRENE® generally shows good resistance to grease and to hydrocarbons. However, polymers become less stable when in contact with polar solvent, ie. hot water, concentrated acids and/or bases, and alcohol above temperatures of 60 °C . Having an enhanced PBT behaviour, harder SIPOLPRENE® grades, show a higher chemical resistance.

CHEMICAL AGENT	CHEMICAL RESISTANCE	
	SOFT GRADES 27-44 Sh D	HARD GRADES 52-72 Sh D
Acetone	🟨	🟨
Benzene	🟨	🟨🟩
Butane	🟩	🟩
Carbon dioxide	🟩	🟩
Carbon monoxide	🟩	🟩
Carbon tetrachloride	🟥	🟨
Chloroform	🟥	🟥🟨
Cyclohexane	🟩	🟩
Ethyl acetate	🟨	🟨
Ethanol	🟩	🟩
Ethylene glycol	🟩	🟩
Formaldehyde, 40%	🟨	🟨
n-hexane	🟩	🟩
Isooctane	🟩	🟩
Isopropyl alcohol	🟩	🟩
Methanol	🟩	🟩
Methyl ethyl ketone	🟨	🟨🟩
Phenol	🟥	🟥
Tetrahydrofuran	🟨	🟨🟩
Toluene	🟨	🟨🟩
Xylene	🟨	🟨🟩
Acetic acid, glacial	🟩	🟩
Nitric acid	🟥	🟥
Formic acid	🟨	🟨
Hydrochloric acid	🟥	🟥
Sulfuric acid > 50%	🟥	🟥
Sodium hydroxide 15%	🟩	🟩
Sodium hydroxide 35%	🟨	🟨
Soap solution	🟩	🟩
Sodium chloride solution	🟩	🟩
Water (70 °C)	🟨	🟨
Water (100 °C)	🟥 🟩 (H- version)	🟥 🟩 (H- version)
Acetylene	🟩	🟩
Freon	🟩	🟩
Hydrogen	🟩	🟩
Gasoline	🟩	🟩
Naphtha	🟩	🟩
Silicone grease	🟩	🟩
Mineral oil	🟩	🟩
Antifreeze solution	🟩	🟩

🟩 = Good resistance. No effect regarding material or its properties
🟨 = Moderate effect regarding material or its properties
🟥 = Not recommended

Fig. 8. SIPOLPRENE® chemical resistance (if not indicated results are referred to tests at room temperature)

FLAME RESISTANCE AND ELECTRICAL PROPERTIES

SIPOLPRENE® has an intrinsically poor flame resistance (HB according to UL 94).
A high dielectric constant together with a good dissipation factor make SIPOLPRENE® suitable for low voltage applications where high mechanical properties and resistance to high temperatures are appreciated over traditional thermoplastics.

SIPOLPRENE® vs OTHER THERMOPLASTIC ELASTOMERS

	SBS	SEBS	TPO	TPV	TPU	SIPOLPRENE® TPC-ET
Density (g/cm³)	0,90 – 1,20	0,90 – 1,20	0,90 – 1,20	0,90 – 1,10	1,10 – 1,40	1,09 – 1,25
Hardness (Shore A/D)	25A – 50D	0A – 60D	60A – 60D	20A – 65D	65A – 70D	25D – 72D
Temperature range of usage (°C)	-50 / 90	-50 / 110	-60 / 110	-50 / 140	-40 / 110	-65 / 185
Compression set (70/100 °C)	■	■ ■	■ ■	■	■ ■	■ ■
Abrasion resistance (mm³)	■	■ ■	■ ■	■ ■	■	■
Hydrocarbons/fat resistance	■	■	■ ■	■ ■	■	■
Non-polar solvent resistance	■	■	■ ■	■	■	■
UV resistance	■ ■	■	■	■	■ ■	■ ■
Strengths	▪ Widely available ▪ Elastic at low T	▪ Widely available ▪ Some grades suitable for food contact	▪ Good performance at low temperature	▪ Wide product range ▪ Good performance / price ratio	▪ Wide product range ▪ Good performance	▪ Excellent resistance to high temperature ▪ Superior resistance to mechanical stress ▪ Good chemical resistance ▪ All grades suitable for food contact
Weaknesses	▪ Low UV and ozone resistance	▪ Low performance / price ratio	▪ Bad elasticity over 60 °C	▪ Limited resistance to hydrocarbons and fat	▪ Low performance / price ratio ▪ Processability	Moderate resistance to: ▪ UV ▪ Ozone ▪ Hydrolysis

■ Bad ■ Moderate ■ Good ■ Excellent

Fig. 9. Comparing different thermoplastic elastomers

MATERIAL PROCESSING

DRYING

SIPOLPRENE® is hygroscopic and therefore it is necessary to dry the granules before use. If the product is exposed to air at room temperature, it absorbs moisture. Moisture, at injection molding temperatures acts as a sort of catalyst for hydrolytic depolymerisation. Thus the lower the moisture content, the higher the quality of the molded parts.

Controlling the moisture content of fresh granules is a key factor to guarantee a good quality in the final molded parts. Therefore, in order to avoid processing problems and loss of mechanical properties, moisture absorption must be avoided as much as possible. During storage, bags and other packaging should be kept sealed and damage free. Pellets which have been exposed to air must be dried before use.

Drying is highly recommended through the use of dry air or nitrogen flowing–ovens. Cycles can vary and depend on drying temperatures. Normally 24 hours at 70-80 °C should be enough. Faster drying cycles can be obtained by increasing the temperature (never beyond 120 °C) for a maximum period of 12 hours. The use of dehumidifiers accelerates the whole drying process.

INJECTION MOLDING GUIDE

Standard injection molding screws can be used. The injected product weight should be in a range between 40% and 70% of the maximum shot capacity, and therefore the machine and relative barrel diameter should be compatible with these values.

The screw should have a L/D ratio of from 17 to 23 and a thread depth ratio of 1:2. A check valve is also recommended.

Nozzles should be short in order to minimize friction and pressure loss.

The hopper must have a tight-fitting lid to keep the pellets dry during processing.

SIPOLPRENE® exhibits good thermal stability at the temperatures required for manufacturing (from 160 to 240 °C).

This minimizes the problem of viscosity decrease during the hold-up time in injection and the formation of degradation byproducts. Besides, SIPOLPRENE®'s thermal properties also make it possible to use a percentage of reground product (e.g. from process scrubs) mixed to virgin ones during injection.

To gain an optimal appearance of molded parts, it is highly recommended to keep the mold temperature between 20 °C and 50 °C depending on wall thickness.

Injection pressure should be set at the minimum required to fill mold cavities. To avoid irregular shrinkage during cooling, higher holding pressures are necessary.

High injection speed allows to achieve good surface finishing and it is recommended for thinner parts. The screw speed should be generally in the range of 30 - 100 rpm.

PRODUCT	MELTING POINT	MOLD T	MELT T	NOZZLE	FRONT ZONE 3	CENTER ZONE 2	REAR ZONE 1
	°C	°C	°C	°C	°C	°C	°C
25170	173	20-30 °C	200	200	190	160	130
25185	184	20-30 °C	210	210	200	170	130
35180	177	20-30 °C	210	210	200	170	130
35195	195	30-40 °C	225	225	215	190	150
46185	186	25-35 °C	220	220	210	175	140
55200	198	30-40 °C	225	225	215	190	150
58210	211	40-50 °C	240	240	220	200	180
63210	211	40-50 °C	240	240	220	200	180
72220	219	40-50 °C	245	240	230	210	200
35150	150	20-30 °C	180	180	170	130	100
40171	170	20-30 °C	200	200	190	160	130
55211	215	40-50 °C	240	240	220	200	180

Fig. 10. General temperature profile for injection molding

2K - MOLDING

The soft nature of SIPOLPRENE® and its chemical structure, which allows to achieve a good adhesion on several rigid engineering plastics products, make it a material of choice in 2K-molding application where "soft touch" is needed and other thermoplastic elastomers do not provide sufficient adhesion.

The table below shows an overview of the adhesion properties of SIPOLPRENE® and other polymers on several substrates.

	PP	PA	PS	ABS	POM	PC	PET	PBT	PVC
SBS	🟩	🟥	🟩	🟥	🟥	🟥	🟥	🟥	🟥
SEBS	🟩	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨
TPO	🟩	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥
TPU	🟥	🟩	🟨	🟩	🟨	🟩	🟥	🟩	🟩
TPV	🟩	🟨	🟥	🟨	🟥	🟨	🟥	🟥	🟥
SIPOLPRENE®	🟥	🟨	🟩	🟩	🟥	🟩	🟨	🟩	🟩

🟥 No adhesion 🟨 Adhesion only with modified grades 🟩 Excellent / good adhesion

Fig. 11. Advantages of SIPOLPRENE® in 2K-molding compared to other elastomers

	TEST METHODS		U.M.	SIPOLPRENE®											
				HIGH PERFORMANCE GRADES									SPECIALTY GRADES		
PROPERTIES	ASTM	ISO		25170	25185	35180	35195	46185	55200	58210	63210	72220	35150	40171	55211
Density	D 792	1183	g/cm³	1,10	1,09	1,12	1,12	1,16	1,19	1,21	1,23	1,25	1,15	1,18	1,21
Hardness (instantaneous)	D 2240	868	Shore D	27	29	35	35	44	52	58	61	72	36	38	54
Strength at break	D 638	527	MPa	23	22	26	21	34	43	48	50	55	28	27	39
Elongation at break	D 638	527	%	800	650	850	700	700	650	500	500	450	600	470	570
Flexural modulus	D 790	178	MPa	30	30	50	50	80	180	250	300	650	50	55	150
Tear strength	D 1004	-	N/mm	85	86	113	115	142	174	207	241	249	100	95	130
Melting temperature	D 3418	3146	°C	173	184	177	195	186	198	211	211	219	150	170	215
Vicat A/50	D 1525	306	°C	73	98	111	137	149	177	186	195	211	105	114	183
Abrasion resistance	D 1044 (Taber H-18 1kg)	-	mg/1000 rev	70	70	60	60	55	45	40	38	38	65	120	90
Water absorption (23 °C x 24 h immersion)	MI / 08		%	0,8	0,8	0,7	0,6	0,5	0,3	0,3	0,2	0,1	0,9	2,8	2,1
MFI 230 °C - 2,16 kg	D 1238	1133	g/10 min	-	-	34	28	34	20	23	23	19	-	-	10
MFI 220 °C - 2,16 kg	D 1238	1133	g/10 min	-	20	-	-	-	-	-	-	-	-	-	-
MFI 200 °C - 2,16 kg	D 1238	1133	g/10 min	12	-	-	-	-	-	-	-	-	-	-	-
MFI 190 °C - 2,16 kg	D 1238	1133	g/10 min	-	-	-	-	-	-	-	-	-	10	8	-
Izod impact strength (notched) (23 °C)	D 256	-	J/m	No break								250	No break		
Izod impact strength (notched) (-40 °C)	D 256	-	J/m	No break					135	50	50	45	No break	15	120

Fig.12. SIPOLPRENE® table of typical properties

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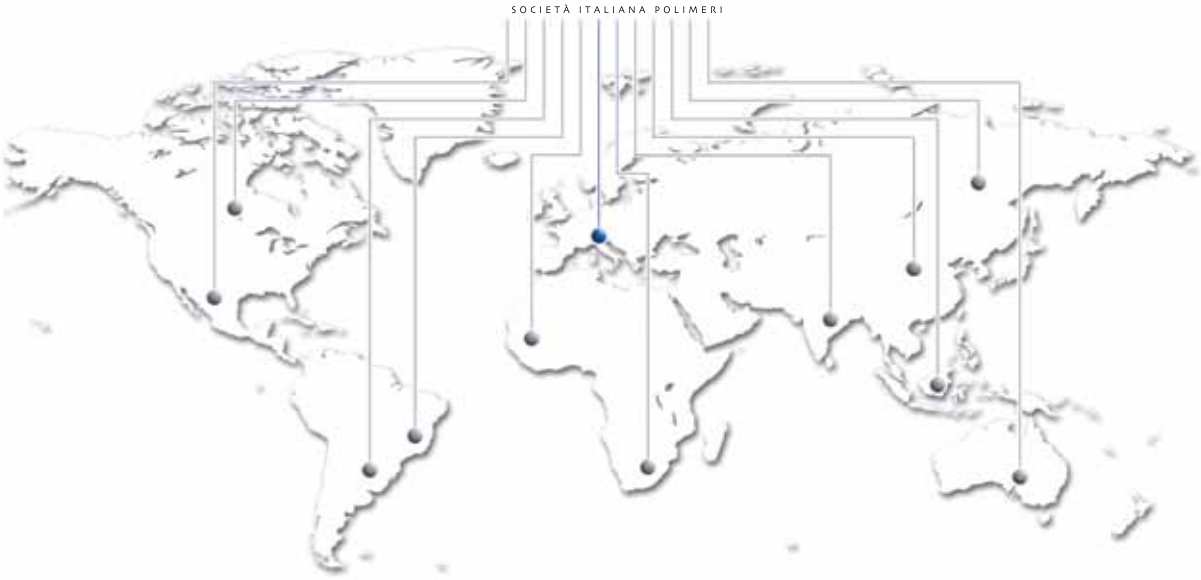

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