High-Performance Polymers
in plastic-rubber composites

FOR A LONG-LASTING MARRIAGE

EVONIK
POWER TO CREATE

We have the right materials to take you to the top

Evonik, the creative industrial group from Germany, is one of the world leaders in specialty chemicals. The company benefits specifically from its innovative prowess and integrated technology platforms. Evonik is active in over 100 countries around the world with more than 35,000 employees.

The High Performance Polymers Business Line focus on manufacturing customized products and systems. For over 50 years, the business line has been producing high performance polymers. With its line of specially modified compounds adhesive-free plastic-rubber composites can be realized in a one- or two-step process achieving cost savings of up to 30% depending on plant-specific conditions.

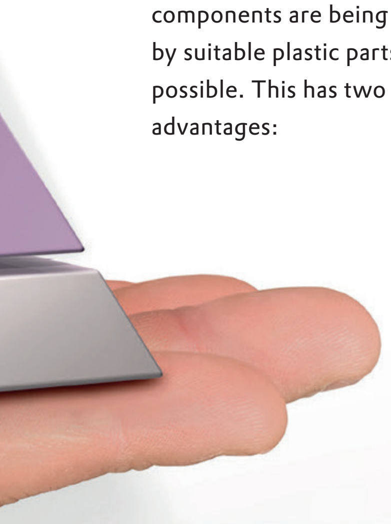
Contents

PLASTIC-RUBBER COMPOSITES

Hard-soft composites

Wherever rubber components must be fastened or fixed, composites consisting of a hard component and an elastomer perform well. They represent an important sector of the rubber industry. Such composites are found in a wide variety of applications, for example, as shock absorbing bearings in the chassis of motor vehicles, buffers or reinforced seals in engines and machines.

Traditionally, hard components consisted of metal composites. To reduce weight, particularly in vehicles, more and more metal components are being replaced by suitable plastic parts wherever possible. This has two additional advantages:



Plastics do not corrode and can be efficiently processed into very complex moldings by injection molding. However, they must be dimensionally stable at the usual vulcanization temperatures of 160 to 190°C. The manufacture of such complex parts from metal is very expensive. The use of plastics in the design of complex components provides the designer and component developer with much greater latitude.

For the long-term function of composites, particularly under dynamic stress, the adhesion between the hard component and the soft component of the composite is an important criterion. It is usually achieved by adhesives. Combinations of all standard rubber types with most metals and simple plastics are possible. Besides additional process steps for applying the adhesives, protective measures against emissions of the usual solvents and their environmentally correct disposal are required.

Adhesion without adhesives

By contrast, the patented plastic-rubber composite process obviates adhesives. Stable, permanent bonds to suitable rubber blends can be produced without pre-treatment using specialty compounds of the VESTAMID® (polyamide 612, polyphthalamide) and VESTORAN® (polyphenylene ether) series.

FIGURE A: The adhesion is based on several mechanisms. When the combination of VESTORAN® and SBR or SBR-containing blends is used, (poly)styrene molecules interdiffuse in the interface. As a result, the substrates are "welded" together.

FIGURE B: The composite of VESTORAN® with peroxidic cross-linked EPDM consists of stable carbon-carbon bonds formed by radicals.

FIGURE C: In the case of the VESTAMID® types, in combination with XNBR, peroxidic cross-linking produces not only carbon-carbon bonds but also amide groups, which ensure permanent adhesion.

The type of the very stable bond of fluororubber to polyamides is not yet completely understood, an ionic reaction with the acid modified rubber could be feasible.

Bonding mechanism

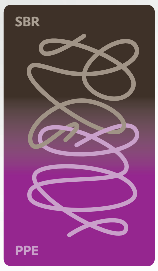


FIGURE A

Bonding of polyphenylene ether to SBR by diffusion of styrene segments

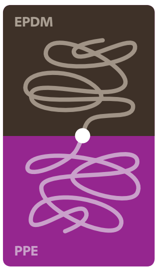


FIGURE B

Radical bonding of polyphenylene ether to EPDM by peroxides

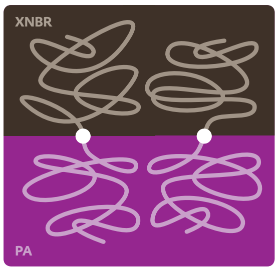


FIGURE C

Radical bonding of polyamides to XNBR by peroxides and amide groups

TWO APPROACHES

Depending on existing technical and plant conditions, two processes are available for manufacturing adhesive-free composites.

Economy

The manufacturing process can be largely automated by eliminating adhesives. Repeated handling of the parts is obviated. Thus, several sources of error are eliminated and the reject rate decreases. Depending on plant-specific conditions, cost savings of up to 30% can be achieved.

For comparing costs between the conventional process and the K&K process, we provide a cost estimate sheet upon request. Simply get in touch with the specified representative.

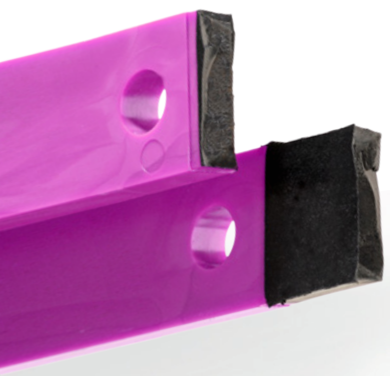
The two-step process

The two-step process is almost identical with the conventional production of rubber-metal and plastic-rubber components. The plastic part is manufactured separately or supplied by an injection molder. The rubber compound is applied to this insert and vulcanized. However, the intermediate step of applying the adhesives is obviated.

This process is particularly useful when the vulcanization time is substantially longer than the cooling time of the associated plastic component. The two process steps can be optimally designed independently of each other. Investments in new machines are not necessary.

The one-step process

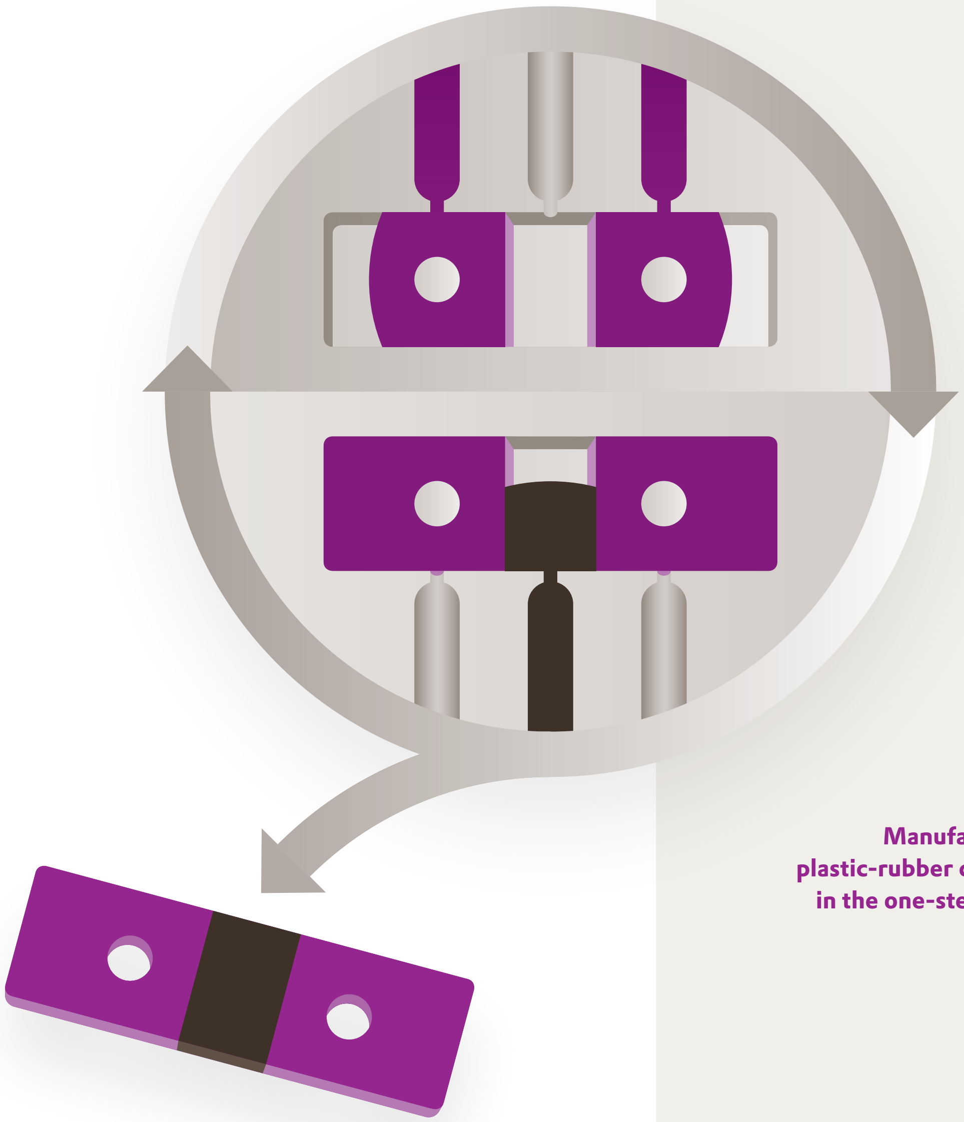
If there is little or no difference between cooling time and vulcanization time, the one-step process is an option. By obviating adhesives, the composites can be manufactured in a common tool without intermediate steps, similarly to the two-component injection molding process. To accomplish this, the injection molding machine must be equipped with a rubber cylinder and a thermoplastic cylinder. Each cavity, that is, the thermoplastic cavity and the rubber cavity, is situated in one half of a common tool. The plastic part is manufactured in the "cold" half of the tool. It is then transferred, for example, with an index plate, transfer handling, or rotation molding into the "hot" half. Here the rubber formulation is applied and vulcanized. At the same time a new plastic molding is formed in the cold half. After the finished composite is dumped from the hot half, the cycle starts again.

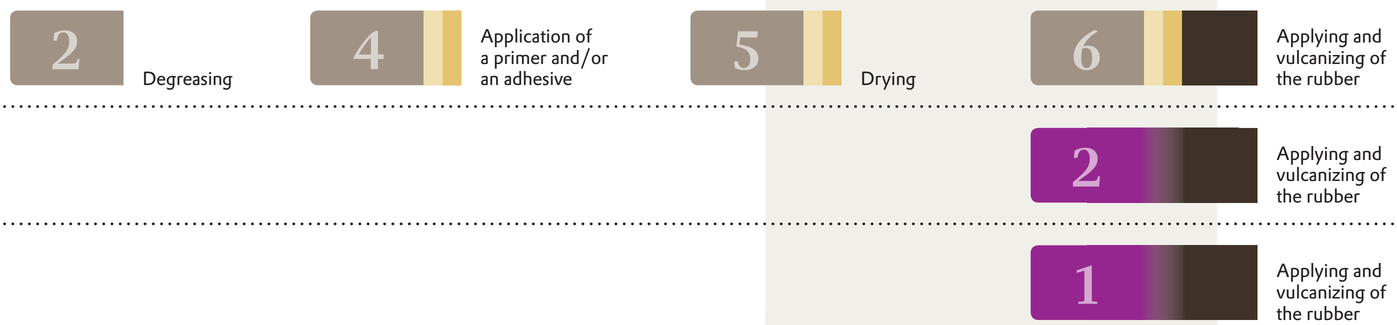


Process steps for composites

CONVENTIONAL PROCESS	Manufacturing of the hard components	1	Temporarily storage
PLASTIC-RUBBER OMPOSITE IN A TWO-STEP PROCESS	Manufacturing of the hard components	1	Temporarily storage
PLASTIC-RUBBER OMPOSITE IN A ONE-STEP PROCESS	Manufacturing of the hard components		

Manufacture of a plastic-rubber composite in the one-step process





SUITABLE COMPOUNDS

Evonik manufactures and sells various polymers suitable for the adhesive-free plastic-rubber composites process.

The polyamide 612 products are named VESTAMID® D, the polyphthalamide (PPA) grades VESTAMID® HTplus, and the polyphenylene ether (PPE) compounds are supplied under the brand VESTORAN®.

Available compounds

Compound	Filler	Combined with	Cross-Linking System	Applications
VESTORAN® 1900				
VESTORAN® 1900GF20	20% glass fibers	SBR, NR/SBR, NBR/SBR, EPDM	Sulfur, peroxide	Vibration absorbers, shock absorbing bushings, reinforced profiles, seals
VESTAMID® X7099	20% glass fibers			
VESTAMID® DX9321	20% glass fibers, impact-modified			
VESTAMID® DX9322	15% ground glass fibers			
VESTAMID® DX9323	35% glass fibers, impact-modified	XNBR, HNBR, AEM, FPM	Peroxide, bisphenol, amine	Oil-resistant seals, moldings, pencil coil ducts, valve flaps
VESTAMID® DX9325	40% glass fibers, impact-modified	EPDM, XNBR, HNBR, AEM, FPM, NBR	Peroxide, bisphenol, amine	Shock absorbing bushings, seals
VESTAMID® HT*plus* R1033	30% glass fibers			
VESTAMID® HT*plus* R1035	50% glass fibers	HNBR, FPM, AEM		
VESTAMID® HT*plus* R1133	30% glass fibers	EPDM, AEM, FPM, HNBR	Peroxide, bisphenol, amine	Heat resistant vibration absorbers, shock absorbing bushings, dumping parts, pencil coil ducts, valve flaps

Combination possibilities

Rubber	VESTORAN® (PPE)	VESTAMID® (PA 612)	VESTAMID® HTplus (PPA)
AEM/ACM	–	A	A
EPDM	P	P	P
FPM	–	BIS/P/A	BIS/P/A
HNBR	–	P	P
NR/SBR	S	–	–
SBR	S	–	–
SBR/NBR	S	–	–
VMQ	–	P	P
XNBR	–	P	–

S = Sulphur, P = Peroxide, A = Amine, BIS = Bisphenol

Polyamides

VESTAMID®

The following Polyamide 612 and Polyphthalamide compounds have been specially developed for plastic-rubber composites:

- *VESTAMID® HTplus R1033*
- *VESTAMID® HTplus R1133*
- *VESTAMID® HTplus R1035*

- *VESTAMID® DX9321*
- *VESTAMID® DX9322*
- *VESTAMID® DX9323*
- *VESTAMID® DX9325*
- *VESTAMID® X7099*

Polyphthalamide
VESTAMID® HT*plus*

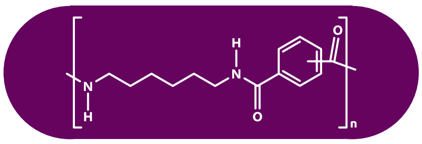
The polyphthalamide VESTAMID® HT*plus* grades suitable for adhesive-free plastic-rubber composites combine high temperature durability, excellent chemical resistance against the most automotive fluids, and outstanding mechanical properties with the flexibility of multiple process technologies. They exploit the high heat deflection temperature of more than 280°C and dimensional stability of VESTAMID® HT*plus*, especially in the range of 120 to 140°C, and add the special functionality of direct bonding to a variety of elastomers.

Compared with PA 66 and PA 612, VESTAMID® HT*plus* features higher strength and stiffness, especially in contact with moisture, a high long-term heat resistance up to 150°C, and a low tendency to creep. Due to higher heat deflection temperature of PPA compared to PA 612 it is possible to vulcanize also thin thermoplastic parts together with rubber up to 190°C without any deformation of the plastic part.

For direct rubber bonding three heat-stabilized grades are available especially developed for manufacturing parts subjected to high temperatures:

- VESTAMID® HT*plus* R1033 and R1133 are 30% glass fiber-reinforced
- VESTAMID® HT*plus* R1035 contains 50% glass fibers.

Moleculare structure
of polyphthalamide



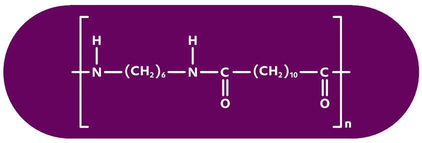
Characteristics
VESTAMID® HT*plus*

Properties			**Test method**	**Unit**	**R1033**	**R1133**	**R1035**
Glass fiber content				%	30	30	50
Density		23°C	ISO 1183	g/cm³	1.43	1.40	1.64
Tensile test							
Tensile strength			ISO 527-1/-2	MPa	180	140	240
Stress at break			ISO 527-1/-2	%	2.0	1.5	2.0
Tensile modulus			ISO 527-1/-2	MPa	11000	10500	17000
CHARPY impact strength*		23°C	ISO 179/1eU	kJ/m²	45 C	29 C	70 C
		-40°C	ISO 179/1eU	kJ/m²	30 C	23 C	50 C
CHARPY notched impact strength*		23°C	ISO 179/1eA	kJ/m²	7 C	6 C	11 C
		-40°C	ISO 179/1eA	kJ/m²	7 C	6 C	11 C
Vicat softening temperature	Method A	10 N	ISO 306	°C	308	300	308
	Method B	50 N	ISO 306	°C	305	275	305
Melt temperature				°C	330 - 340	330 - 340	330 - 340
Mold temperature				°C	140 - 180	140 - 180	140 - 180
Temperature of deflection under load	Method A	1.80 MPa	ISO 75-1	°C	290	270	290
	Method B	0.45 MPa	ISO 75-2	°C	305	295	305

*C = complete break

Polyamide 612
VESTAMID® D

As partially crystalline materials, VESTAMID® PA612 compounds for adhesive-free rubber composites feature excellent chemical resistance, particularly toward greases, oils and fuels. Besides very good sliding friction properties, PA 612 compounds show appreciably less water absorption than PA 6 or PA 66.



Moleculare structure of polyamide 612

Chemical resistance

The chemical resistance of PA 612 is comparable to that of PA 12. Polyamide 612 generally displays outstanding resistance to fuels, lubricants, greases, oils, and most industrial solvents. Polar solvents can cause reversible swelling, especially at elevated temperatures. This will generally be connected with a drop in strength (plasticizer effect). In practice, the original characteristics will be restored after the solvent has evaporated. Liquids that have a particularly high affinity to the carbonamide groups of the polyamides can act as solvents for PA 612 at higher temperatures. Examples are phenols, cresols, benzyl alcohol, and particular chlorohydrocarbons.

Due to their low water absorption, PA 612 compounds exhibit very good resistance to aqueous agents, such as alkali solutions, saline solutions, and cleaners. Their resistance to aqueous acids is limited, depending on the temperature, time, and concentration.
In general, concentrated acids will lead to a more or less rapid drop in relative molar mass (embrittlement). Concentrated sulfuric acid and formic acid will dissolve PA 612.

Rubber combinations

Compounds with different glass fiber contents and, in some cases, with impact modification are available. For manufacture of oil-resistant and fuel-resistant seals and moldings, they can be combined with appropriate rubber blends, for example, based on XNBR rubber, partially saturated HNBR rubber and FPM rubber.

Moldings for the two-step plastic-rubber process should be stored in a dust-free atmosphere and processed within three months.

Properties

PHYSICAL, MECHANICAL AND
Density
Tensile test
Stress at yield
Strain at yield
Stress at break
Strain at break
Tensile modulus
CHARPY impact strength*¹
CHARPY notched impact strength*¹
Vicat softening temperature
Melt temperature
Mold temperature
Temperature of deflection under load
Linear thermal expansion
Mold shrinkage
Flammability acc. UL94
Water absorption
Moisture absorption
ELECTRICAL PROPERTIES
Relative permittivity
Dissipation factor
Electric strength
Comparative tracking index
Volume resistivity

*¹ N = no break, C = complete break

Characteristics
VESTAMID® D

		Test method	Unit	DX9322 black 15% milled glass fibers	X7099 black 20% glass fibers	DX9321 black 20% glass fibers	DX9323 black 35% glass fibers	DX9325 black 40% glass fibers
THERMAL PROPERTIES								
	23°C	ISO 1183	g/cm³	1.17	1.20	1.19	1.31	1.41
		ISO 527-2/1 A	MPa	63				
		ISO 527-2/1 A	%	8				
		ISO 527-2/1 A	MPa	59	120	115	140	164
		ISO 527-2/1 A	%	18	6	5	5	5
		ISO 527-2/1 A	MPa	3150	5500	5700	8300	10200
	23°C	ISO 179/1eU	kJ/m²	46 C	95 C	93 C	104 C	100 C
	-30°C	ISO 179/1eU	kJ/m²	43 C	80 C	106 C	110 C	104 C
	23°C	ISO 179/1eA	kJ/m²	4 C	13 C	18 C	20 C	17 C
	-30°C	ISO 179/1eA	kJ/m²	3 C	8 C	11 C	15 C	16 C
Method B	50 N	ISO 306	°C	194	208	207	209	
			°C	240 - 280	230 - 270	240 - 280	240 - 280	240 - 280
			°C	30 - 100	30 - 100	30 - 100	30 - 100	30 - 100
Method A	1.80 MPa	ISO 75-1/-2	°C	114	195	189	196	195
Method B	0.45 MPa	ISO 75-1/-2	°C	186	212	208	213	210
longitudinal	23°C - 55°C	ISO 11359	$10^{-4}K^{-1}$	1.0	0.5	0.5	0.5	0.5
transverse	23°C - 55°C	ISO 11359	$10^{-4}K^{-1}$	0.6	0.7	0.7	0.8	
in flow direction		ISO 294-4*²	%	1.92	0.55	0.66	0.35	0.19
in transverse direction		ISO 294-4*²	%	0.93	1.05	0.88	1.02	0.68
	1.6 mm	IEC 60695		HB	HB	HB	HB	HB
	3.2 mm	IEC 60695			HB		HB	HB
	23°C, saturation	ISO 62	%	2.4	2.0	2.0	1.9	1.9
	23°C, 50 % r.F.	ISO 62	%	0.9	0.8	0.8	0.8	0.8
	100 Hz	IEC 60250		4.3	4.4	4.4	4.8	
	1 MHz	IEC 60250		3.1	3.9	3.1	3.6	
	100 Hz	IEC 60250	10^{-4}	430	650	500	610	
	1 MHz	IEC 60250	10^{-4}	493	430	470	320	
	K20/P50	IEC 60243-1	KV / mm		38		39	
Test solution A	CTI	IEC 60112		> 600		> 600	> 600	
Test solution A	100 drops value	IEC 60112		575		600	575	
		IEC 60093	Ohm • cm	10^{14}	10^{13}	10^{14}	10^{14}	

*² Specimen 60 x 60 x 2 mm

Polyphenylene Ether

VESTORAN®

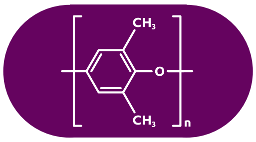
Four grades of the amorphous poly-2,6-dimethyl-1,4-phenylene ether VESTORAN® are available for adhesive-free plastic-rubber composites:

- *VESTORAN® 1900 natural*
- *VESTORAN® 1900 black*
- *VESTORAN® 1900 GF20 light ivory*
- *VESTORAN® 1900 GF20 black*

Polyphenylene Ether
VESTORAN®

VESTORAN® grades can be combined with SBR and SBR blends, such as NR/SBR; the SBR portion should be at least 20 wt%. These rubbers are to be cross-linked with sulfur. Applications of such combinations include vibration bushings and shock absorbers in the chassis of motor vehicles. Combinations with EPDM compounds that are peroxidically cross-linked perform well. Examples of applications are reinforced profiles and seals.

VESTORAN® has high heat deflection temperature. Moldings of VESTORAN® have very low mold shrinkage and warpage. VESTORAN® is hot water resistant. The water absorption is very low.



Moleculare structure of polyphenylene ether

Chemical resistance

PPE is resistant to alkalis and acids but less resistant to fats, oils and fuels. The stress cracking susceptibility test according to ISO 4599 under the influence of different media is a criterion for chemical resistance (bent strip test, 3.5% outer fiber strain with basic grades; 2.7% outer fiber strain in the case of glass fiber-reinforced grades). The resistance is dependent on temperature but also on the stress state of the test specimen. Therefore, we recommend using a test under field conditions to determine whether the requirements are met.

Chemical resistance VESTORAN®

Medium		Test temperature (°C)	Basic grades	Glass fiber-reinforced grades
	50%	80	+	+
Acetic acid	100%	20	–	–
Acetone		20	–	–
Ammonia	25%	20	+	+
	50%	100	+	+
Antifreeze	100%	100	+	+
Brake fluid (ATE DOT 4)		20	–	–
Cyclohexane		20	–	–
	50%	20	+	+
Diethylene glycol	99%	20	+	+
1,4-Dioxane		20	–	–
Ethanol		20	+/–	+/–
Ethyl acetate		20	–	–
Ethylene glycol		20	+	+
	80%	20	+	+
Formic acid	100%	20	+	+
Glycerin		20	+	+
Hydraulic fluid (Shell Tegula 32)		20	–	–
	10%	20	+	+
Hydrochloric acid	35%	20	+	+
Isobutanol		20	+/–	+/–
Isopropanol		20	+/–	+/–
Lubricating oil (BP Energrease)		80	–	–
Methanol		20	+/–	+/–
Methyl ethyl ketone		20	–	–
Methyl-tert.-butyl ether (MTB)		20	–	–
Motor oil SAE 15-W40		80	–	–
N,N-Dimethylformamide		20	–	–
Nitric acid	65%	20	–	–
Oxalic acid	5%	80	+	+
Paraffin oil		20	+	+
	10%	20	+	+
Phosphoric acid	85%	20	+	+
	10%	20	+	+
Potassium hydroxide solution	60%	20	+	+
		20	+	+
Silicone oil 740		80	+	+
	10%	80	+	+
Sodium hydroxide solution	50%	20	+	+
	10%	80	+	+
	25%	20	+	+
Sulfuric acid	98%	20	–	–
Toluene		20	–	–
Water		100	+	+

+ resistant +/– somewhat resistant – not resistant

Polyphenylene Ether

VESTORAN® – Characteristics

Characteristics
VESTORAN®

Properties			Test method	Unit	VESTORAN® 1900	VESTORAN® 1900GF20
PHYSICAL, MECHANICAL AND THERMAL PROPERTIES						
Density		23°C	ISO 1183	g/cm³	1.04	1.19
Melt volume-flow rate (MVR)		300°C/21.6 kg	ISO 1133	cm³/10 min	ca. 40	ca. 20
Tensile test						
Stress at yield			ISO 527-1/-2	MPa	60	
Stress at yield			ISO 527-1/-2	%	6	
Tensile strength			ISO 527-1/-2	MPa		100
Strain at break			ISO 527-1/-2	%	>50	3
Tensile modulus			ISO 527-1/-2	MPa	2000	5600
Flexural modulus			ISO 178	MPa	2400	5700
CHARPY impact strength*		23°C	ISO 179/1eU	kJ/m²	250 P	50 C
CHARPY notched impact strength*		23°C	ISO 179/1eA	kJ/m²	25 C	12 C
Temperature of deflection under load	Method A	1.80 MPa	ISO 75-1/-2	°C	170	185
	Method B	0.45 MPa	ISO 75-1/-2	°C	190	190
Vicat softening temperature	Method A	10 N	ISO 306	°C	190	200
	Method B	50 N	ISO 306	°C	185	190
Flammability acc. UL94		0.8 mm	ISO 60695		HB	HB
		1.6 mm	ISO 60695		HB	HB
Water absorption		23°C, saturation	ISO 62	%	0.4	0.4
Processing shrinkage	in flow direction		ISO 294-4	%	approx. 0.9	0.5
	in transverse direction		ISO 294-4	%	approx. 0.8	0.6
ELECTRICAL PROPERTIES						
Relative permittivity		100 Hz	IEC 60250		2.6	2.9
		1 MHz	IEC 60250		2.9	2.7
Dissipation factor		100 Hz	IEC 60250		$8 \cdot 10^{-4}$	$8 \cdot 10^{-4}$
		1 MHz	IEC 60250		$16 \cdot 10^{-4}$	$18 \cdot 10^{-4}$
Electric strength		K20/P50	IEC 60243-1	kV/mm	40	33
Comparative tracking index	Test solution A	CTI	IEC 60112		225	200
	Test solution A	100 drops value	IEC 60112		200	175
Volume resistivity			IEC 60093	Ohm • m	10^{13}	10^{13}
Surface resistance R_{OA}			IEC 60093	Ohm	10^{14}	10^{13}
Electrolytic corrosion			IEC 60426	Stage	A1	A1

*P = partial break, C = complete break

Polyphenylene Ether
VESTORAN® – Processing

Pre-drying

Although VESTORAN® absorbs very little moisture, pre-drying in a circu-lating or vacuum dryer is extremely important.

To prevent damage to the material, drying conditions should not exceed 110 to 120°C for 2 hours. The pre-dried granulate must be introduced hot into the machine hopper. The dwell time of the melt in the cylinder should be less than 5 minutes.

Mold

Externally heated hot runner systems must be used. Approximately 0.05 mm deep venting channels should be placed near the welding lines.

Temperature settings for separate manufacture of the moldings (two-step process):

VESTORAN® 1900 .... 80 to 90°C
VESTORAN® 1900 GF 20 .... 130 to 140°C

Temperature settings for the one-step process:

VESTORAN® 1900 .... 180°C
VESTORAN® 1900 GF 20 .... 180°C

The higher mold temperature in the one-step process enables the molding heat to be utilized for a shorter vulcanization time of the rubber component. An exhausting device above the injection molding machine is strongly recommended.

Handling VESTORAN® moldings in the two-step process:

When pre-molded components are used for the plastic-rubber composites, no mold release agents may be used. The VESTORAN® surfaces must be free of grease and dust. Intermediate storage of the moldings is done in the dark, for example, in black polyethylene bags. Further processing within two weeks is recommended. Contaminated surfaces can be cleaned by wiping them off with toluene.

Machine parameters

Screw

L/D ratio min. 20:1
Compression ratio 2:1 to 3:1

Nozzle

Diameter greater than 3 mm

Injection pressure

800 to 1600 bar

Holding pressure

50 to 80% of injection pressure

Temperature settings

Cylinder: 280 / 300 / 320 / 320°C
Nozzle: 310°C
Melt: 300 to 330°C

The melting temperature should not exceed 340°C to prevent thermal damage to the PPE.

Interested in plastic-rubber technology?

Involve us in your projects.
Get in touch. Talk with your local representative or contact:

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