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High Performance Polymers



THE RUBBER WITH UNIQUE PROPERTIES



Synthesis of VESTENAMER

VESTENAMER

The rubber with unique properties

The demands on rubber products have been increasing steadily. Likewise, the requirements on rubber compounds have become more and more exacting as well. Many rubber compounds, however, have poor processing properties that cannot be improved by conventional processing aids. This is where VESTENAMER trans-polyoctenamer, which has been well established for years, has proved itself as a valuable processing aid. Due to its properties, it is a versatile polymer that can be used to solve a wide variety of problems dealing with rubber compounding and processing.

Synthesis and structure of VESTENAMER

The monomer feedstock of VESTENAMER is cyclooctene, which is synthesized from 1,3-butadiene via 1,5-cyclooctadiene. Cyclooctene is polymerized to polyoctenamer (TOR) in a metathesis reaction that produces both linear and cyclic macromolecules (Figure 1). The cis/trans ratio, which determines the degree of crystallinity of TOR, is controlled by the polymerization conditions. Two VESTENAMER grades of different crystallinity—8012 and 6213—are commercially available. The unique and exceptional properties of VESTENAMER are characterized by four structural features:

- **Crystallinity**
- **Low viscosity above the melting point**
- **High proportion of macrocycles**
- **Double bond content**



Synthesis

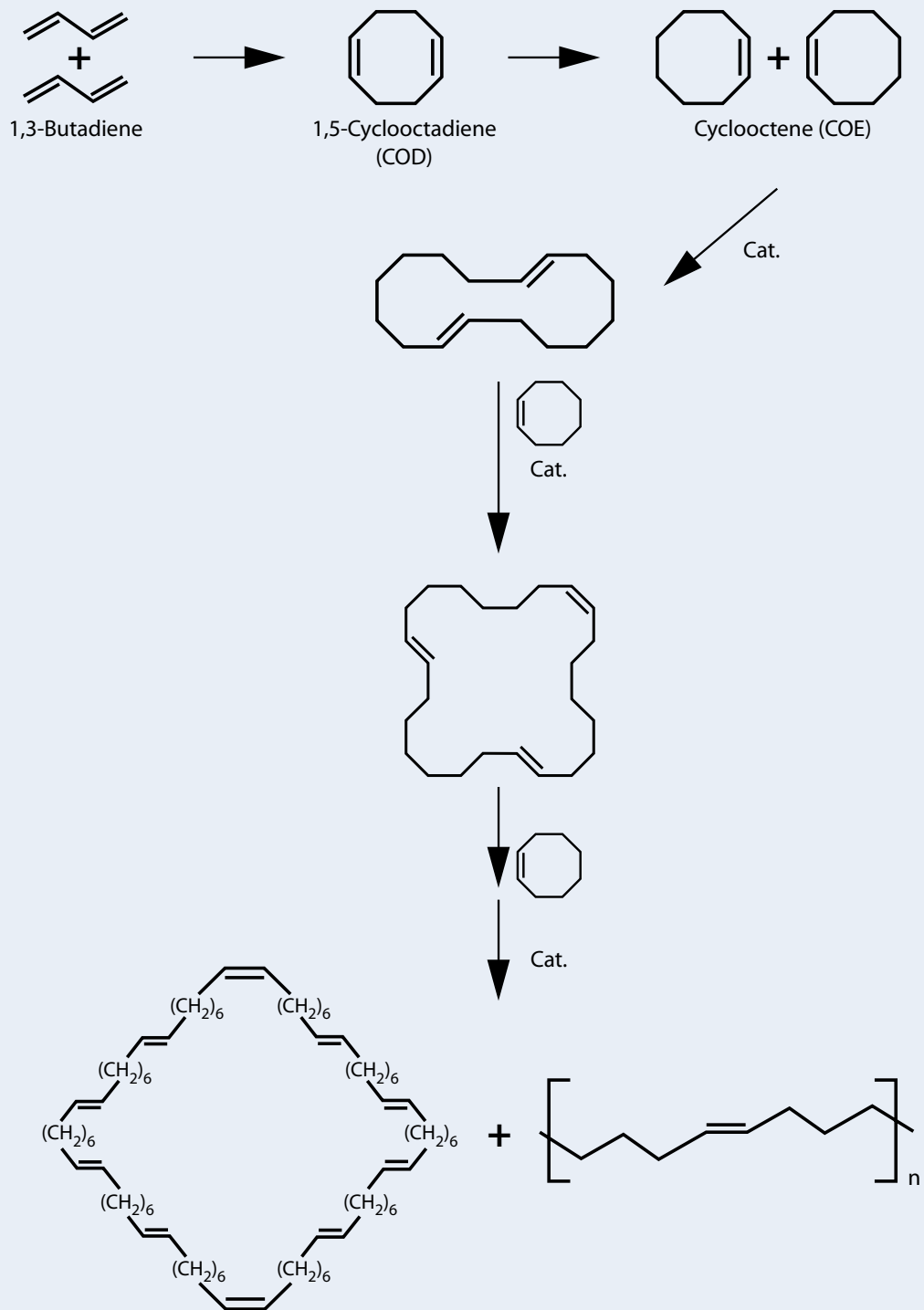


Figure 1

Properties

Properties

Crystallinity

As mentioned above, the cis/trans ratio of the double bonds in polyoctenamer determines the degree of crystallinity. In general, if trans-content is increased, a higher crystallinity is produced and thus a higher melting point can be obtained. The crystallinity is thermally reversible, and the crystallization rate is exceptionally high. This effect can be used to reduce the cold flow of, e.g., soft compounds, to improve collapse resistance in profile extrusion, increase the hardness of vulcanizates, and reduce the shrinkage and its anisotropy in calendaring.

Low viscosity above the melting point

The high content of macrocycles permits a considerable reduction of the molecular weight, since macrocycles, in contrast to linear macromolecules, can form a completely three-dimensional network on cross-linking, even at a low molecular weight. This low molecular weight, in combination with a broad molecular weight distribution, also accounts for the exceptionally low viscosity at elevated temperatures. At temperatures above the melting point, both VESTENAMER grades are low viscous melts with Mooney values (100 °C) below 10. Thus the plasticizing effect of VESTENAMER improves the processing of rubber compounds in many ways (Figure 2).

High proportion of macrocycles

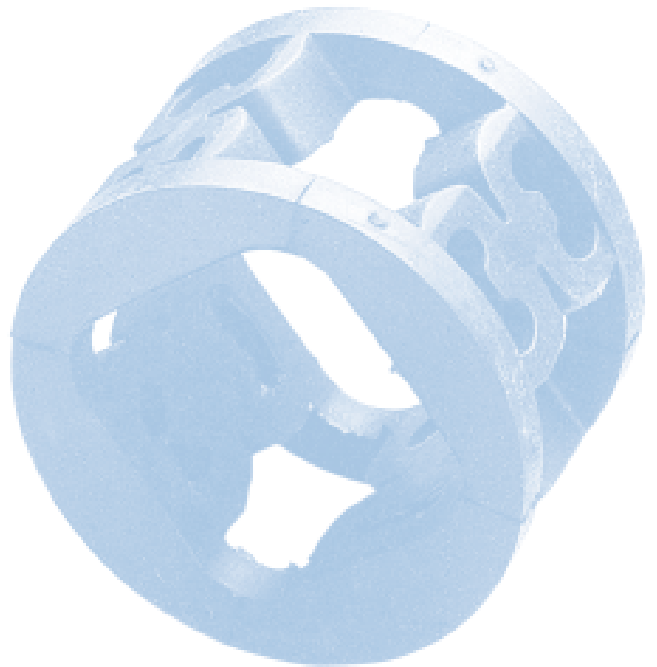
VESTENAMER contains at least 25 weight-% of macrocycles with a molecular weight of up to 100,000. These macrocycles presumably account for the high collapse resistance of VESTENAMER-containing rubber compounds at temperatures well above its melting point. This is certainly the result of entanglements between the linear molecules of the basic rubber and the macrocycles of VESTENAMER. These cyclic macromolecules have a further influence on the physical properties of the vulcanizates, e.g., by increasing the rebound resilience. On the other hand, the lack of end groups in the macrocycles and the remaining, completely unbranched linear molecules significantly reduce the tack of uncured rubber compounds. Depending on the application, this can be a negative effect, e.g., in natural rubber compounds, or a positive effect as in the case of polychloroprene compounds.





Double bond content

On metathesis polymerization, the double bond of cyclooctene is preserved so that the resulting trans-polyoctenamers contains a double bond at every eighth carbon atom. Due to the degree of unsaturation, the cure rate is somewhat lower than for SBR. VESTENAMER vulcanizes with all cross-linking agents commonly used in rubber curing, e.g., sulfur, sulfur donors, peroxides or curing resins.



Polymer compatibility and mixing technique

VESTENAMER is compatible with almost all rubbers, irrespective of their chemical structure or polarity. It can even compatibilize polymers that are otherwise incompatible, such as EPDM and NBR or emulsion- and solution-rubbers. In general, VESTENAMER is applied in a blend by substituting 5 to 15 parts of the base polymer. In special cases, the dosage may be higher. With few exceptions, VESTENAMER is fed into an internal mixer or an open mill together with the base polymer. It facilitates and accelerates filler incorporation, improves filler dispersion and reduces energy consumption as well as dump temperature and compound viscosity.



Influence

Influence of VESTENAMER on rubber processing

Influence of VESTENAMER on vulcanizate properties

The physical properties of VESTENAMER-containing compounds are determined by the TOR content. In general, hardness and modulus are increased, whereas tensile strength, elongation at break and tear resistance are slightly decreased. The dynamic properties are improved as demonstrated by the reduced heat built-up in fatigue tests. Thermal and UV stability is better than for SBR. The ozone resistance of EPDM is not impaired. Swelling is similar to EPDM or SBR, and abrasion resistance nearly matches polybutadiene.



VESTENAMER applications

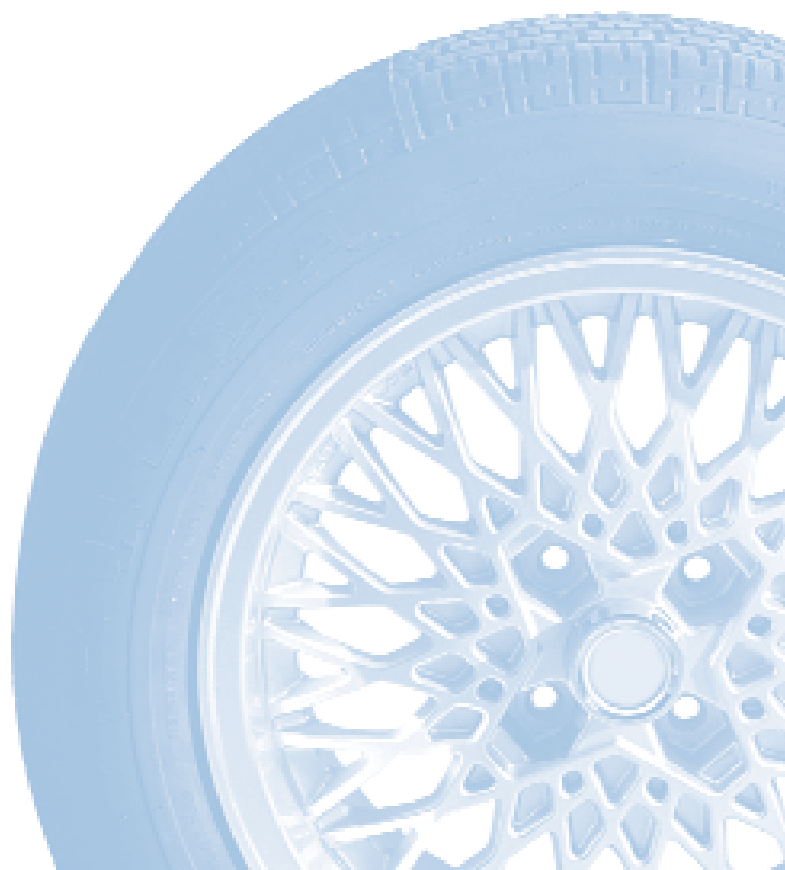
The combination of properties described above expresses the dual character of VESTENAMER: during processing it has the function of a plasticizer and processing aid, but after cross-linking it is a rubber. Hence, it is mainly utilized in the rubber industry to improve the processability of rubber compounds without the disadvantages presented by traditional processing aids. The particular benefits of VESTENAMER in major applications shall be described below.

Extrusion

Flowability is improved by VESTENAMER, resulting in a higher output of precise extrudates and improved surface finish. With TOR it is possible to process very hard compounds (e.g., without plasticizer) that otherwise cannot be processed at all or only with great difficulty. The better collapse resistance afforded by TOR also improves the dimensional stability of profiles. The increasing hardness you obtain with decreasing temperature can be a benefit in hose production, where the lining often has to be cooled for braiding. Hence cooling time can be reduced to obtain the required hardness.

Injection molding

The application of VESTENAMER improves the molding of large and voluminous parts as well as high precision parts. Moreover, it allows very hard compounds with originally poor flow properties to be injection-molded. Due to the enhanced flowability, cycle times can be reduced.



Influence

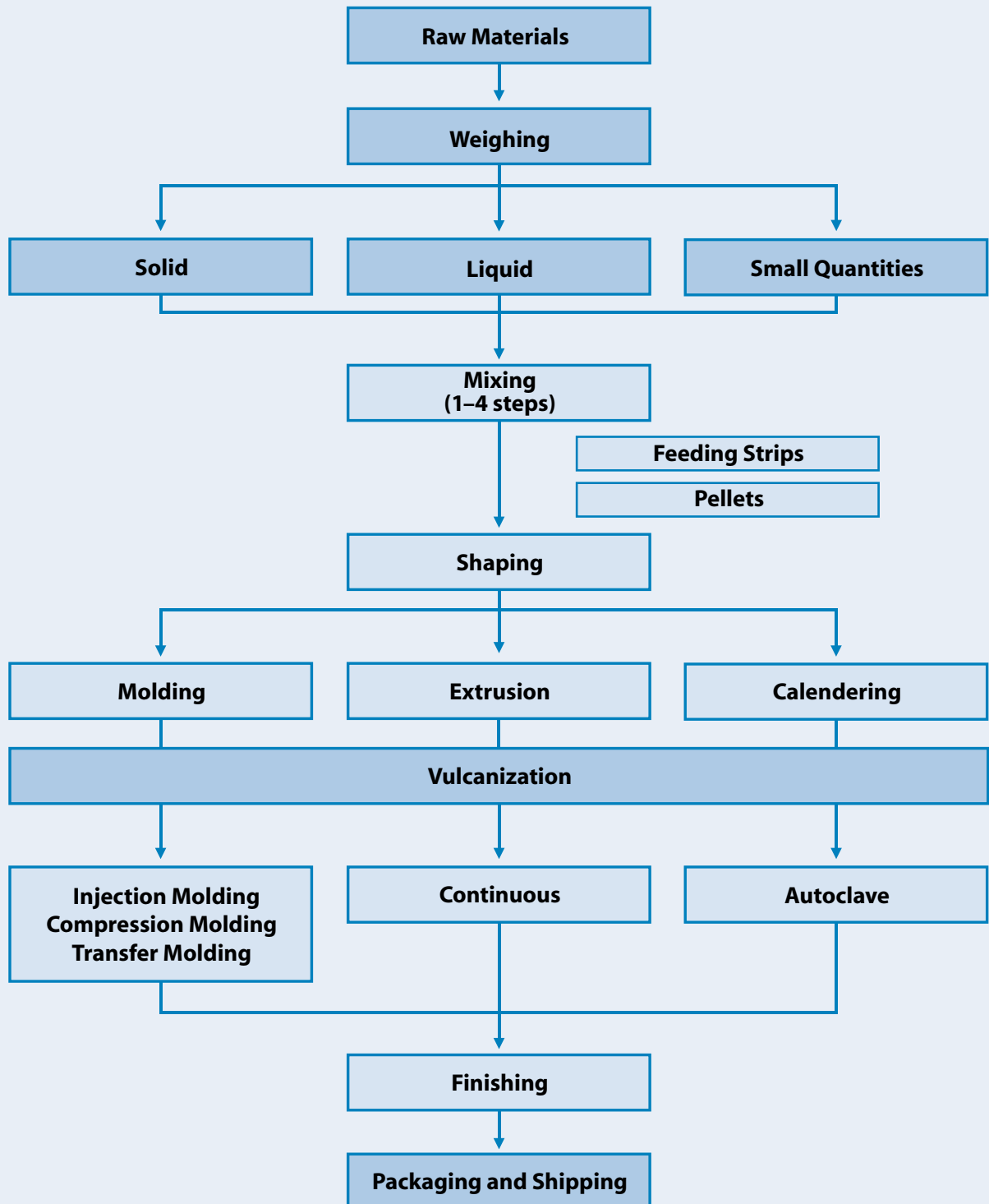


Figure 2

Influence

Influence of VESTENAMER on rubber processing



Calendering

VESTENAMER reduces shrinkage and anisotropy of calendered sheets and improves surface finish and fabric penetration. The sheeting of dry shoe sole compounds is facilitated. The increased green strength makes roll covering easier, whereas the good flowability improves layer welding and prevents flow marks.

Tire production

Tire production represents an important and diverse range of applications for VESTENAMER. To build a tire, ten to fifteen different compounds are necessary. Many of these compounds have special requirements for which TOR can be useful to solve processing or handling problems. For very thin tire parts, such as sidewall or rim strips, TOR prevents deformation or over-stretching, thanks to its high green strength. On the other hand, it improves—by its plasticizing effect—the processing of very hard compounds with high carbon black loadings, such as bead and apex compounds. Here the application of reinforcing resins is limited because of their negative influence on the dynamic properties. VESTENAMER, however, combines improved mixing and processing while enhancing dynamic properties.

Rubber recycling

VESTENAMER can easily be dissolved in mineral oils at elevated temperatures. Ground rubber waste can be reprocessed by simply coating the crumbs in inexpensive equipment with an oil-VESTENAMER solution and additional curatives. These “activated” rubber crumbs can either be molded into rubber goods directly or can be added to fresh rubber compounds as a reactive filler. Compared to uncoated crumb, the physical properties of the finished parts are improved by VESTENAMER.

Based on our experience with rubber recycling, we found a new application for VESTENAMER in connection with ground tire rubber in asphalt concrete production. High quality pavements can be prepared by mixing the VESTENAMER with ground tire rubber and asphalt cement. Small amounts of VESTENAMER disperse fillers efficiently, promoting compatibility and cross-linking in rubberized asphalt mixtures. In addition, it reduces the high tackiness of these rubberized mixtures. This allows for an earlier compacting of the asphalt concrete with steel and rubber rollers at higher temperatures, which saves time and money. This ability of VESTENAMER to cross-link the ground tire rubber to the asphalt creates a rubberized matrix in the asphalt paving that prevents premature cracking, rutting and shoving. For further information, see our brochure “VESTENAMER Reactive Modifier.”



Influence

Batch technology

Due to its distinct thermoplasticity and low melting point, VESTENAMER can be used for the production of polymer-bound masterbatches of chemicals, both for plastics and rubber compounds. This is especially true for the preparation of masterbatches containing thermally sensitive chemicals, such as peroxides, accelerators and blowing agents. VESTENAMER, e.g., in combination with EP(D)M or EVA, serves as a carrier because of its good filler incorporation. Due to the high crystallization rate and level, the batches can easily be granulated for handling, and undesired tack is suppressed. On the other hand, the low viscosity above its melting point allows fast and easy dispersion of the chemicals.

Modification of thermoplastics

Because of its unique characteristics, VESTENAMER can also be used as an impact modifier in thermoplastics. In the production of thermoplastic rubbers based on polyolefines, TOR can compatibilize the different raw materials and activates the dynamic cross-linking through peroxides.



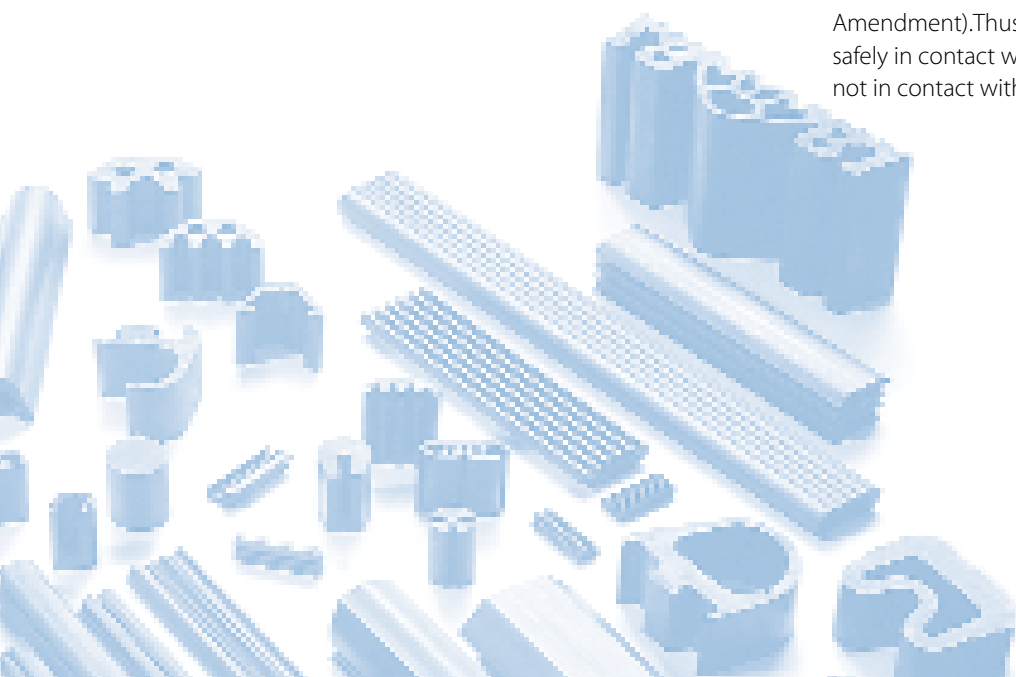
Toxicological properties

VESTENAMER has an LD 50 value of >12,500 mg/kg in rats (oral) and has no irritating effect on the skin or on rabbits' eyes.

In rats, 90-d oral administration at concentrations up to 4,000 mg/kg body weight did not result in any toxic effects.

VESTENAMER showed no mutagenic effects in the Ames test on *Salmonella typhimurium* (in vitro) and the micronucleus test (in vivo) on mice.

The Scientific Committee on Food of the European Commission evaluated cyclooctene for food contact and approved it for use in aqueous foodstuffs (restriction: specific migration limit SML: 0.05 mg/kg). Cyclooctene will be added to Section A of the Positive List for Monomers of the EU-Plastics Directive 90/128/EEC (6th Amendment). Thus VESTENAMER can be used safely in contact with aqueous foodstuffs (but not in contact with alcoholic and fatty foods).



Property	Method	Unit	VESTENAMER Grade	
			8012	6213
Molecular weight, M_w	GPC	–	90,000	110,000
Glass transition temperature, T_g	ISO 6721 ISO 4663	°C	–65	–75
Crystallinity at 23 °C	DSC (2nd melting)	% (appr.)	30	10
Melting point	DSC (2nd melting)	°C	54	<36
Thermal decomposition	TGA	°C	275	250
cis/trans ratio of double bonds	IR	%	20:80	40:60
Mooney viscosity ML (1+4) 100 °C	DIN 53 523 ASTM-D 1646	–	<10	<10
Viscosity number J/23 °C	ISO 1628-1	ml/g	120	130
Ash content	DIN 53 568, part 1 ISO/DIS 3451-1	%	max 0.1	max 0.1
Volatile matters (1h/105 °C)	DIN 53 526 ISO 248	%	max 0.5	max 0.5
Stabilizer	–	–	sterically hindered phenol, non staining	
Density	DIN 53 479 A ISO 1183	g/cm ³	0.91	0.89
Apparent density	ISO 60	g/l	560	550
Appearance/ delivery form	–	–	light, opaque pellets	



Tables

Property	Method	Unit	VESTENAMER Grade		
			8012	6213	
MVR 190/2.16 ¹⁾	ISO 1133	cm ³ /10 min	18	13	
MVR 190/5	ISO 1133	cm ³ /10 min	50	36	
MVR 230/2.16	ISO 1133	cm ³ /10 min	28	18	
MVR 230/5	ISO 1133	cm ³ /10 min	78	50	
Stress at yield	ISO 527-1	MPa	7.5	–	
Strain at yield	ISO 527-1	%	25	–	
Stress at break	ISO 527-1	MPa	8.5	1.2	
Strain at break	ISO 527-1	%	400	300	
Charpy impact strength –20 °C	ISO 179/1eU	kJ/m ²	no break	no break	
Tensile impact strength	23 °C	ISO 8256	kJ/m ²	165	38
	0 °C	ISO 8256	kJ/m ²	190	36
	–20 °C	ISO 8256	kJ/m ²	240	34
Isod notched impact strength	23 °C	ISO 180/1 A	kJ/m ²	no break	–
	0 °C	ISO 180/1 A	kJ/m ²	22	–
	–23 °C	ISO 180/1 A	kJ/m ²	19	–

¹⁾ MVR = Melt Volume Flow Rate

Thermogravimetric analysis (TGA)

a) Under nitrogen, heating rate 10 °C/min Weight loss (%)			b) Under air, heating rate 10 °C/min Weight loss (%)		
up to (°C)	of 8012	of 6213	up to (°C)	of 8012	of 6213
300	0.60	0.73	300	0.47	1.19
400	2.03	2.56	400	1.18	2.35
425	2.83	3.40	425	1.30	2.55
450	9.47	14.66	450	6.78	7.20
475	60.59	71.85	475	98.01	96.84
500	99.08	98.71	500	98.39	97.36
525	99.87	98.85	525	99.00	98.15
550	99.95	98.87	550	99.53	98.88

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VESTENAMER®

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