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Description

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Polyethylene molding composition/

5 The invention relates to a polyethylene molding composition which consists of two different types of polyethylene and is suitable for the production of gas pipes, landfill belts and sheets with very good characteristics.

10 The preparation of blends from high density polyethylene (HDPE) and linear low density polyethylene (LLDPE) for the preparation of moderate density polyethylene (MDPE) in order to obtain molding compositions with improved characteristics is known (cf. GB 843,697, GB 860,329, GB 944,208, US 4,374,227, CA 1,106,521). The high density polyethylene used in these blends has a monomodal molecular mass distribution.

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It has now been found that the characteristics of polyethylene blends can be further improved if the high density polyethylene used is a high density polyethylene having a bimodal molecular mass distribution.

20 The invention therefore relates to a polyethylene molding composition having a density (23°C) of 0.930 to 0.940 g/cm³ and a MFI 190/2.16 of 0.05 to 1.0 g/10 min, consisting of 50 to 80 % by weight of a HD polyethylene having a density (23°C) of 0.940 to 0.960 g/cm³, a MFI

25 190/2.16 of 0.01 to 0.5 g/10 min and a broad bimodal molecular mass distribution and 20 to 50 % by weight of a polyethylene having a low density (23°C) of 0.910 to 0.930 g/cm³ and a MFI 190/2.16 of 0.5 to 2.0 g/10 min.

30 The polyethylene molding composition according to the invention consists of a high density polyethylene (HDPE) and a low density polyethylene, preferably a linear low



density polyethylene (LLDPE).

The HD polyethylene has a density (23°C) of 0.940 to 0.960, preferably 0.940 to 0.950 g/cm³ and a MFI 190/2.16 of 0.01 to 0.8, preferably 0.1 to 0.5 g/10 min. It also
5 has a very broad bimodal molecular mass distribution and can contain small proportions of propylene, but-1-ene, pent-1-ene or hex-1-ene monomer units.

The bimodality can be described as a measure of the position of the centers-of-mass of the two individual
10 molecular mass distributions with the aid of the coefficients of viscosity (CV according to ISO/R 1191) of the polymers formed in the two polymerization stages. The CV₁ of the polyethylene formed in the first stage is 40 to 80 cm³/g and the CV of the end product is in the range
15 from 270 to 330 cm³/g. The CV₂ of the polyethylene formed in the second stage can be calculated from the following equation:

$$CV_2 = \frac{CV_{\text{end product}} - w_1 CV_1}{1 - w_1}$$

20

where w_1 is the proportion by weight (% by weight) of the ethylene polymerized in the first stage, with respect to the total ethylene polymerized in both stages. CV₂ is as a rule 480 to 580 cm³/g.

25 The HD polyethylene is obtained by suspension, solution or gas phase polymerization of ethylene, optionally in the presence of small amounts of C₃- to C₈-1-olefins, at a temperature of 20 to 120°C and under a pressure of 2 to 60 bar in the presence of a Ziegler catalyst, which
30 consists of a transition metal compound and an organo-aluminum compound. The polymerization is carried out in two stages. The molecular mass is controlled with the aid of hydrogen.

The proportion of hydrogen in the gas space of the first reactor is 80 ± 5 % by volume and that in the gas space of the second reactor is 6 ± 4 % by volume.

5 A typical example for the preparation of a suitable HD polyethylene is described below:

10 A catalyst is first prepared. To this end, 114.3 g of magnesium ethylate are dispersed in 1 dm³ of a diesel oil fraction, under N₂ blanketing, in a 3 l four-necked round bottom flask fitted with a dropping funnel, a precision glass stirrer, a reflux condenser and a thermometer. 474 g of titanium tetrachloride are added dropwise to this dispersion, while passing through a gentle stream of N₂, in the course of 2 h at 100°C. The reaction mixture is then washed at 100°C with diesel oil until the super-
15 natant solution contains no further titanium. 38 g of titanium tetrachloride are now added dropwise at 140°C in the course of 1 h and the batch is stirred for a further 60 h while passing a gentle stream of N₂ over the mixture. The reaction product is then washed with the
20 abovementioned diesel oil fraction until the supernatant solution contains no further titanium.

After drying, the solid (component A) has approximately the following analytical composition:

25 Ti 5.1 % by weight
Mg 20.8 % by weight
Cl 71.7 % by weight

30 39.9 g of component A are suspended in 150 cm³ of diesel oil, and 100 cm³ of an isoprenylaluminum solution, which contains 0.5 mol of isoprenylaluminum/dm³, are added at 20°C with stirring. About 35 % by weight of the tetravalent titanium is reduced to titanium(III) by this means.





This catalyst component is used in a continuous two-stage process for the polymerization of ethylene.

Typical operating data are (Table 1):

5		Reactor 1 (120 dm ³)	Reactor 2 (120 dm ³)
	Temperature	83°C	83°C
10	Catalyst feed	2.5 mmol/h	15 mmol/h
	Dispersant (diesel oil)	25 dm ³ /h	50 dm ³ /h
15	Ethylene	7 kg/h	8 kg/h
	Hydrogen in the gas space	80 % by volume	6 % by volume
20	Total pressure	10 bar	2.5 bar

A polymer prepared under these operating conditions using triisobutylaluminum as cocatalyst had the following product characteristics:

25	Powder:	coefficient of viscosity (ISO R 1191)	300 cm ³ /g
		MFI 190/5	0.65 g/10 min
		MFI 190/2.16	0.19 g/10 min
		density (23°C)	0.944 g/cm ³ /g
	Granules:	MFI 190/5	0.45 g/10 min
30		MFI 190/2.16	0.12 g/10 min
		density (23°C)	0.94 g/cm ³ /g

The low density polyethylene has a density (23°C) of 0.910 to 0.925, preferably 0.915 to 0.925 g/cm³ and a



MFI 190/2.16 of 0.5 to 2.0 g/10 min. Preferably, a linear low density polyethylene (= LLDPE) having a narrow, uni-modal molecular mass distribution is used. Small amounts of other monomer units which are derived from propylene, but-1-ene, pent-1-ene, hex-1-ene, hept-1-ene or oct-1-ene or 4-methylpent-1-ene can be incorporated in the polymer chain.

Suitable linear low density polyethylenes (LLDPE) are obtained by polymerization using transition metal catalysts. They are commercially available. Suitable products are listed in Table 2.

	Preparation process	Density (23°C) g/cm ³	MFI 190/2.16 g/10 min
Product 1	Low pressure (LLDPE)	0.923	1.15
Product 2	"	0.920	1.0
Product 3	"	0.919	0.88 .
Product 4	"	0.919	1.02
Product 5	"	0.917	0.89
Product 6	High pressure (LDPE)	0.924	0.99

A suitable high pressure low density polyethylene is also available commercially. It is also listed in Table 2.

The HD polyethylene to LD polyethylene ratio in the molding composition according to the invention is 50:50 to 80:20, preferably 60:40 to 75:25.



In addition to the polyethylenes, the molding composition according to the invention can also contain the customary additives, for example a) heat stabilizers, antioxidants, UV absorbers, light stabilizers, metal deactivators, compounds which destroy peroxide and basic costabilizers and b) fillers, reinforcing agents, plasticizers, lubricants, emulsifiers, pigments, fluorescent brighteners, flame retardants, antistatic agents or propellants.

The various additives of the abovementioned group a) are added to the molding composition in an amount of from 0.01 to 10, preferably 0.01 to 5 % by weight, based on the total weight of the molding composition. The proportion of the additives of group b) is 1 to 80, preferably 10 to 50 % by weight, based on the total molding composition.

The molding composition according to the invention is prepared by the methods customary for processing plastics, for example by granulating granule/granule or granule/powder mixtures with the possible addition of additives.

The molding composition has a density (23°C) of 0.930 to 0.940 g/cm³ and a MFI 190/2.16 of 0.05 to 1.0, preferably 0.1 to 1.0 g/10 min and meets the requirements for a thermoplastic material classified P23 in accordance with ASTM D 1248 having a yield stress > 18 MPa (> 12 MPa in accordance with ASTM D 1248 and measured in accordance with DIN 53455) and an elongation at break of > 700 % (> 400 % in accordance with ASTM D 1248 and measured in accordance with DIN 53455) and a brittleness temperature of < -60°C (measured in accordance with ASTM D 746). The material also displays exceptional resistance to slow crack propagation (ESCR).

The pipes produced from the molding composition using conventional processes have excellent characteristics:



processing very good

pipe surface very good

Mechanical properties:

Young's modulus (DIN 53475) $\approx$ 620 MPa

- 5 notched impact strength $a_n \approx$ 15-35 mJ/mm² at 0°C
 (DIN 53453 U-notch)

Long-term characteristic (stress-rupture PN10 32/3 mm pipe)

according to DIN 8075

- 10 service life ($\sigma =$ 4 MPa, 80°C) $>$ 5000 h

The invention is illustrated in more detail by the following examples.

Example 1

- 67 parts by weight of powder of a HD polyethylene having
15 a bimodal molecular mass distribution, 33 parts by weight
 of granules of a but-1-ene/4-methylpent-1-ene/ethylene
 terpolymer (product. 1) having a unimodal molecular mass
 distribution, 0.05 part by weight of pentaerythritol
 tetrakis[3-(3,5-di-t-butyl-4-hydroxyphenyl)-propionate],
20 0.1 part by weight of tris(2,4-di-t-butylphenyl) phos-
 phite and 0.2 part by weight of Ca stearate were mixed
 and granulated under blanketing inert gas using a twin-
 screw extruder (D = 53 mm, L = 10 D; T = 210-240°C).

The polymer data were:

- 25 HDPE: Density = 0.944 g/cm³
 MFI 190/2.16 = 0.23 g/10 min
 MFI 190/5 = 0.70 g/10 min
 LLDPE: Density = 0.923 g/cm³
 MFI 190/2.16 = 1.15 g/10 min
30 MFI 190/5 = 3.18 g/10 min

Test pieces were prepared from the granules and the tests indicated in Table 3 were carried out. The results are also summarized in Table 3.



Example 2

65 parts by weight of granules of a HD polyethylene having a bimodal molecular mass distribution, 35 parts by weight of granules of an oct-1-ene/ethylene copolymer (product 2) having a unimodal molecular mass distribution and the stabilizers according to Example 1 were mixed and processed to granules analogously to Example 1.

10 HDPE: Density = 0.944 g/cm^3
MFI 190/2.16 = 0.16 g/10 min
MFI 190/5 = 0.62 g/10 min
LLDPE: Density = 0.920 g/cm^3
MFI 190/2.16 = 1.0 g/10 min
MFI 190/5 = 3.15 g/10 min

The test results are summarized in Table 3.

15 Example 3

65 parts by weight of powder of a HD polyethylene having a bimodal molecular mass distribution, 35 parts by weight of granules of an oct-1-ene/ethylene copolymer (product 2) having a unimodal molecular mass distribution and the stabilizers according to Example 1 were mixed and processed to granules analogously to Example 1.

25 HDPE: Density = 0.944 g/cm^3
MFI 190/2.16 = 0.2 g/10 min
MFI 190/5 = 0.80 g/10 min
LLDPE: Density = 0.920 g/cm^3
MFI 190/2.16 = 1.0 g/10 min
MFI 190/5 = 3.15 g/10 min

The test results are summarized in Table 3.

Example 4

30 PN10 pipes were produced from the molding compositions according to Examples 1 to 3 on a pipe installation. The machine data were:

Extruder D = 48 mm, L = 24.4 D

Die mandrel $\varnothing$ 26.5 mm, orifice $\varnothing$ 32.1 mm

Vacuum calibration

Cooling bath length 3 m, temperature about 15°C

- 5 The target temperature in the extruder was 200°C. The extruder was operated at various speeds of rotation and the throughput, the mass pressure and the mass temperature were measured. The values are summarized in Table 4.

Example 5

- 10 The pipes produced in accordance with Example 4 were subjected to a stress-rupture test in accordance with DIN 8075. The service lives were as follows for the pipes produced from the molding composition
according to Example 1 > 4800 h,
15 according to Example 2 > 5000 h and
according to Example 3 > 4000 h.

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Table 3

Characteristic		Test method	Example 1	Example 2	Example 3
Density	g/cm ³	DIN 53479	0.938	0.935	0.935
CV	cm ³ /g	ISO/R 1191	290	270	260
MFI 190/2.16	g/10 min	DIN 53735	0.23	0.30	0.31
MFI 190/5			0.93	1.13	1.15
MFI 190/2.16			18.2	19.0	18.6
MFR 21.6/5			19.6	16.8	16.2
Young's modulus	MPa	DIN 53457-t	643	636.4	618.4
Flexural creep modulus	MPa	DIN 54852 (1 min)	804	766	751
Yield stress	MPa	DIN 53455 ISO/R 527 125 mm/min Test piece 3	19.9	18.7	18.6
Elongation at yield stress	%		9.1	11.6	10.3
Tear strength	MPa		38.6	34.7	37.5
Elongation at break	%		793.7	740.0	749.7
a _n	23°C	Notched impact strength U-notch DIN 53453 (Pressed standard small rod)	18.8	n.f.**	n.f.**
	0°C		16.1	28.6	36.6
	-20°C		10.4	13.2	13.5
Bell test 100°C	h	ASTM D 1693 C	> 1000	> 1000	> 1000
Tear test 80°C*	h	5 MPa, glycol	379 ± 128	> 2000	> 2000
OIT 200°C	min	ISO/IC 138	48	28.5	23.6

* Resistance to stress cracking: service life of samples of square cross-section notched all round

** No fracture



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Table 4

			Example 1	Example 2	Example 3
5	n=50 min ⁻¹	T _m	°C	221	223
		P	bar	115	110
		Q	kg/h	21.7	22.1
10		N/Q	kWh/ kg	0.203	0.214
15	n=80 min ⁻¹	T _m	°C	227	228
		P	bar	135	135
		Q	kg/h	34.5	35.2
20		N/Q	kWh/ kg	0.209	0.207
25	n=110 min ⁻¹	T _m	°C	231	233
		P	bar	155	155
		Q	kg/h	47.4	47.1
30		N/Q	kWh/ kg	0.219	0.22

n speed of rotation

Q throughput

P mass pressure

35 T_m mass temperature

N power consumption

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Patent claims

1. A polyethylene molding composition having a density (23°C) of 0.930 to 0.940 g/cm³ and a MFI 190/2.16 of 0.05 to 1.0 g/10 min, consisting of 50 to 80 % by weight of a HD polyethylene having a density (23°C) of 0.940 to 0.960 g/cm³, a MFI 190/2.16 of 0.01 to 0.5 g/10 min and a broad bimodal molecular mass distribution and 20 to 50 % by weight of a polyethylene having a low density (23°C) of 0.910 to 0.925 g/cm³ and a MFI 190/2.16 of 0.5 to 2.0 g/10 min.
2. The polyethylene molding composition as claimed in claim 1, wherein the low density polyethylene is a linear LD polyethylene having a narrow unimodal molecular mass distribution.
3. The polyethylene molding composition as claimed in claim 1, which has been prepared by mixing and granulating the constituents.



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