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(54) Title: ELASTOMERIC COMPOUND

(57) Abstract: The invention relates to an elastomeric compound comprising at least one olefinic elastomer comprising ethylene, an α-olefin, from 1 to 7 wt% vinyl norbornene and from 0 to 15 wt% of a second non-conjugated polyene, wherein the wt% are related to the total weight of ethylene, α-olefin, vinyl norbornene and the second non-conjugated polyene, and which elastomer has long chain branching corresponding with $\Delta\delta$ <20, wherein $\Delta\delta$, expressed in degrees, is calculated from the difference between the phase angle δ between stress and strain in a dynamic shear measurement at 125°C at a frequency of 0.1 rad/s and the phase angle δ at a frequency of 100 rad/s and the compound further comprising a solid filler and an oil, such that the compound has a compound loading between 120 and 300 phr, wherein said olefinic elastomer satisfies the following relation $S_b > 30$, wherein S_b is the slope in a graph of $\ln(a_c)$ versus Φ, in which a_c is the factor along which the low frequency part ($\omega < 1$ rad/s) of the phase angle δ versus ω plots, measured at at least one volume fraction Φ between 0.2 and 1 of the olefinic elastomer in squalane, must be shifted to coincide with a δ versus ω plot of an undiluted polymer (Φ =1), and wherein the δ versus ω plots results from a frequency sweep performed on a stress controlled rheometer carried out at 125 °C under nitrogen atmosphere, using a parallel plate geometry in shear. The invention further relates to a method for the preparation of the compound of the invention.

ELASTOMERIC COMPOUND

The invention relates to an elastomeric compound comprising at least one olefinic elastomer comprising ethylene, an α-olefin, from 1 to 7 wt% vinyl norbornene and from 0 to 15 wt% of a second non-conjugated polyene, wherein the wt% are related to the total weight of ethylene, α-olefin, vinyl norbornene and the second non-conjugated polyene, and which elastomer has long chain branching corresponding with $\Delta\delta$ <20, wherein $\Delta\delta$, expressed in degrees, is calculated from the difference between the phase angle δ between stress and strain in a dynamic shear measurement at 125°C at a frequency of 0.1 rad/s and the phase angle δ at a frequency of 100 rad/s and the compound further comprising a solid filler and an oil, such that the compound has a compound loading between 120 and 300 phr.

The invention further relates to the preparation of an elastomeric compound suitable for extrusion and to extruded parts made from such compound.

Elastomeric polymers are generally processed in the form of a compound, wherein the polymer is mixed with fillers like carbon black and/or oil. Consequently, the processing of such a compound can be considered as processing of a solution of the polymer rather than processing of a melt thereof.

Typical phenomena that may occur when a polymer is extruded through a die are die swell and surface distortions such as sharkskin, slip-stick or even gross melt fracture. Compounds suitable for extrusion should not require high torques and pressures during processing and should not be prone to surface distortions.
It is known that lower viscous products generally give rise to improved extrusion behavior. It is further known that, for elastomeric polymers with a certain Mooney viscosity, improved extrusion behavior can be achieved by selecting grades with long-chain branches. The amount of branching is expressed in terms of a $\Delta\delta$-parameter as described by Booij in Kautschuk und Gummi Kunststoffe, (1991), 44:2, p128-130. In this article it has been shown that a lower value of $\Delta\delta$ indicates that the polymer has a higher amount of long chain branching. Consequently, elastomer polymers having low values of $\Delta\delta$ are preferably selected for making compounds suitable for a high throughput in extruding e.g. profiles. However, the polymerization/production of such highly branched polymers brings the risk of creating gel particles, which is undesirable.

Another requirement for a compound with good extrusion behavior is that it cures fast and to a high level. This can be obtained by an as high as possible level of vinyl norbornene in the elastomeric polymer. From WO2005/005496 it is known that elastomeric polymers can be made that include a high amount of VNB with a relatively low risk of forming gel particles by using a specific catalyst system based on a single site organometallic compound and an aluminoxane activator.

It is an object of this invention to provide an elastomeric compound that combines a high VNB concentration with an improved throughput during extrusion, in the substantial absence of extrudate distortion and with no or substantially no gel particles being present.

We have surprisingly found that a compound according to claim 1 exhibits an improved throughput during extrusion without extrudate distortions.

The elastomeric compound according to the invention comprises:

a) At least one olefinic elastomer comprising ethylene, an α-olefin, from 1 to 7 wt% vinyl norbornene and from 0 to 15 wt% of a second non-conjugated polyene, wherein the wt% are related to the total weight of ethylene, α-olefin, vinyl norbornene and the non-conjugated polyene. Ethylene and α-olefin amounts preferably range respectively between 50 and 75wt% for ethylene and between 20 and 50 wt% for propylene.
b) The elastomeric compound according to the invention further has a compound loading of between 120 and 300 phr, which means that in addition to 100 phr of the olefinic elastomer, the compound further comprises 20 to 200 phr of other compounding ingredients of which at least an oil, a solid filler, and a curing package.
c) The olefinic elastomer in the compound of the invention generally has a long chain branching long chain branching corresponding with $\Delta\delta$ <20, wherein $\Delta\delta$, expressed in degrees, is calculated from the difference between the phase angle δ between stress and strain in a dynamic shear measurement at 125°C at a frequency of 0.1 rad/s and the phase angle δ at a frequency of 100 rad/s.
d) The olefinic elastomer in the compound of the invention further satisfies the following relation $S_b > 30$, wherein is the dilution slope S_b, as described in the experimental part.

The dilution slope S_b is a parameter described as $g_\varnothing$ by B. J. Crosby, M. Mangnus, W. de Groot, R. Daniels and T. C. B. McLeish in "Characterization of long chain branching: Dilution rheology of industrial polyethylenes", Journal of

Rheology -- March 2002 -- Volume 46, Issue 2, pp. 401-426 to characterize the branching architecture of polymers from their solution properties.

The inventors surprisingly found that compounds according to the invention based on olefinic elastomers or a blend of olefinic elastomers with a dilution slope of more than 30, preferably more than 32, even more preferably more than 34 and most preferable more than 35, show significant lower surface instabilities during extrusion, which directly results in a higher throughput during extrusion without surface instabilities.

The compound of the invention preferably comprises, in addition to the olefinic elastomer,

a) a solid filler. Suitable solid fillers to be used in the compound of the invention are e.g. carbon black, silica, whiting, aluminum and magnesium silicates, quartz, chalk, and talk, said filler present in said olefinic elastomer compound in the range of from 10 to 190 parts, preferably from 10 to 100 parts per hundred parts olefinic elastomer(phr),

b) from 10 to 190 phr, preferably from 10 to 100 parts of an oil e.g. parafinic oil or white oil.

Compounds in the above-mentioned range show a significant lower die swell and reduced extrudate distortions. Below a compound loading of 120 phr the effect of the compound loading on the extrusion behaviour is negligible. Above a compound loading of 300 phr the effect of the olefinic elastomer in the compound is too limited.

Another advantage of the compound of the invention is, that at a certain level of long chain branching of the olefinic elastomer, corresponding to a certain $\Delta\delta$, the amount of VNB in the olefinic elastomer is much higher than for the known VNB comprising olefinic elastomers. This results in a higher cure rate, and higher crosslink density for the olefinic elastomers according to the invention. The advantage of a higher crosslink density is expressed in better compression set properties.

A further advantage of the compound of the invention is, that these compounds are substantially free of gel particles.

The olefinic elastomer in the compound according to the invention preferably has a Mooney viscosity [ML(1+4)125°C] in the range of from 20 to 130. An elastomer with a Mooney viscosity of more than 20 comprises a sufficient amount of branches to obtain the effect of the invention. The effect of the invention above a

Mooney viscosity value of 130 is not excluded, but economically unattractive because of reactor fowling during production of the elastomeric polymer. An ML(1+4)125^{0}C) is difficult to measure above a value of about 90. Above an ML(1+4)125°C the Mooney value is preferably measured at 150°C. An upper limit of 130 ML(1+4)125^{O}C corresponds with a ML(1+4)150^{0}C of about 90 MU.

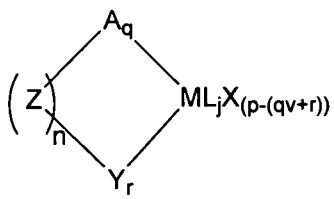
The effect of the invention at low compound loadings is most pronounced if the polymer Mooney viscosity (ML(1+4)125°C) lies in the range from 60 to 90 MU.

The invention further relates to a method for the preparation of a compound according to claim 1. This method is characterized by the features of claim 3.

The invention further relates to an extruded part comprising the cured compound of the invention. An extruded part comprising the cured compound of the invention can be obtained by adding to the compound a sufficient amount of a known curing agent, after which the mixture is extruded and cured by methods known to somebody skilled in the art.

WO2005/005496 discloses that the type of catalyst can have a strong influence on the amount of long chain branching. This invention shows that modifications of the ligands within the group of single site catalysts according to formula 1, may even influence the type of long chain branches.

A suitable olefinic elastomer to be used in the compound of the invention can be prepared by polymerizing at least ethylene, an alpha-olefin, between 1 and 7 wt%, preferably 1.5 – 5 wt%, more preferably 2 – 4 wt% of vinyl norbornene and optionally between 0 and 15 wt% of a second non-conjugated monomer in the presence of a catalyst system comprising:
a metal-organic compound of the following formula:

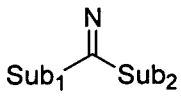


(formula 1)

where:
M is a metal of group 3 –13 or the lanthanide series, and p is the valency of the metal M;

A represents a neutral or anionic spectator ligand whose valency v is 0,1 or 2, and q is an integer denoting the number of spectator ligands A;
Z is an optional bridging moiety, and n is the integer number of parallel bridging moieties Z;

Y is an amidine-containing spectator ligand represented by formula 2:



(formula 2),

wherein the amidine-containing ligand is covalently bonded to the metal M via the imine nitrogen atom, Sub_1 is a substituent, which comprises a group 14 atom through which Sub_1 is bonded to the imine carbon atom. Sub_2 is a substituent, which comprises a heteroatom of group 15-16, through which Sub_2 is bonded to the imine carbon atom,;
r is an integer > 0;
L is an optional neutral Lewis basic ligand, and j is an integer denoting the number of neutral ligands L, and
X is an anionic ligand that may be independently selected from the group consisting of hydride, halide, alkyl, silyl, germyl, aryl, amide, aryloxy, alkoxy, phosphide, sulfide, acyl, pseudo halides such as cyanide, azide, and acetylacetonate, or a combination thereof.
and a cocatalyst comprising an aluminoxane.

Preferably the compound according to formula 2 is (NC(2,6-F_2Ph)(^{i}Pr_2N). With the catalyst based on this ligand, an elastomeric polymer can be produced with 3.5 wt% of VNB and a S_b of more than 40.

Experimental methods

Determination of the Mooney viscosity

The measurement of Mooney viscosity, i.e. Mooney viscosity ML_{1+4} (125°C)], is defined according to the standard ASTM D-1646, herein incorporated by reference. In ASTM D-1646, it is stated that the Mooney viscosity is not a true viscosity, but a measure of shearing torque over a range of shearing stresses. Measurement of Mooney viscosity is also described in the Vanderbilt Rubber Handbook, 13th Ed., (1990), pages 565-566.

Determination of $\Delta\delta$

The phase angle δ between stress and strain in a dynamic shear measurement was determined as a function of the angular frequency ω in between 10^{-1} and 100 rad/s on a stress-controlled rheometer (MCR300, Paar-Physica). All measurements were performed at 125°C under a nitrogen atmosphere, using a parallel plate geometry (diameter and gap of respectively 25 mm and 1.5 mm) in shear at strain amplitudes below 15%.

For the undiluted elastomer $\Delta\delta$, expressed in degrees, is calculated from the difference between the phase angle δ at a frequency of 0.1 rad/s and the phase angle δ at a frequency of 100 rad/s [H.C. Booij, Kautschuk + Gummi Kunststoffe, Vol. 44, No. 2, pages 128-130, 1991].

Determination of the dilution slope S_b

Rheological measurements (frequency sweeps) were performed on a stress-controlled rheometer (MCR300, Paar-Physica). All measurements were performed at 125°C under a nitrogen atmosphere, using a parallel plate geometry (diameter and gap of respectively 25 mm and 1.5 mm) in shear.

At strain amplitudes below 15%, the phase angle δ between stress and strain and the ratio of the stress and strain amplitudes, i.e. the dynamic shear modulus G_d, were determined as a function of the angular frequency ω in between 10^{-4} and 100 rad/s. These measurements were carried out on different volume fractions (Φ) of the elastomer between 100 (i.e. the undiluted elastomer) and about 20 % in a squalane solvent.

Solutions were prepared by first dissolving the sample material in an excess of white spirit. In order to homogenize this solution, the mixture was stirred for 24 hours with a magnetic stirrer. Then the required amounts of squalane were added to obtain the different volume fractions. Finally, all traces of white spirit were removed by placing the mixtures under vacuum at 70 °C for 48 hours. Squalane ($C_{30}H_{62}$), a short chain alkene, was chosen as solvent due its high boiling temperature (T_{boil} = 200 °C). White spirit (T_{boil} = 35 °C) was used as a co-solvent to facilitate the dissolving process of the polymer and thereby improving the homogeneity of the dilutions.

The dilution slope is determined from dynamic mechanical measurements on solutions having polymer volume fractions such that the phase angle at 0.0001-0.1 rad/s lies in the range of 60-90 degrees. For this purpose, at least three

polymer concentrations are required (typically for high Mooney polymers between 10 and 50 wt% of polymer in solvent and for low Mooney polymers typically between 50 and 90 wt% of polymer.).

According to Crosby B.J., Mangnus M., de Groot W., Daniels R. and McLeish T.C.B., "Characterization of long chain branching: Dilution rheology of industrial polyethylenes, J. Rheol., 46(2), 401-426 (2002) the low frequency part ($\omega <$ 1rad/s) of the curves of δ versus ω can be shifted along the logarithmic frequency axis (using a shift factor a_c) to coincide with each other. For this purpose, the curve at the highest volume fraction of the polymer is selected as reference. The natural logarithm of the shift factor a_c, thus determined, satisfies the following relation: $\ln(a_c) = S_b \cdot \Phi$, where S_b is the dilution slope and ϕ the volume fraction of elastomer. The dilution slope is determined by linear regression of $\ln(a_c)$ vs. Φ.

Polymer used

Polymers 1- 8 and 10

Olefinic elastomers used in the Comparative Examples are commercial graded from DSM (polymers 1- 8 and 10).

Polymers 9 (105173b)

Polymer 9 was made according to the described polymerisation procedure on lab scale using a Vanadium based Ziegler Natta catalyst. A VOCl3 solution in hexane was fed into the reactor and ethylaluminium sesquichloride (SEAC) solution in hexane was fed into the pre-cooled monomer stream. The molar ratio between VOCl3 and SEAC was 8 and the reactor temperature was 45°C.

Polymer 11 (04289a)

Polymer 11 was made according to the described polymerisation procedure on lab scale using catalyst A.

Description catalyst A:

η^5-(perfluorophenylcyclopentadienyl)(tri-*tert*-butylphosphinimine) titanium dimethyl.

To an orange mixture of $C_6F_5CpTiCl_3$ (1.00 g, 2.59 mmol) and *t*-Bu_3PClNH_2 (0.68 g, 2.59 mmol) in toluene (60 mL) and THF (20mL) was added a

MeMgBr solution in ether (3.0M, 4.0 mL, 12 mmol) at –20°C. The reaction mixture was stirred for 45 minutes and subsequently dried in vacuo. The residue was extracted with boiling ligroin (20 and 40 mL respectively). The solvents were removed in vacuo resulting in 1.33 g (98%) of $(Cp\text{-}C_6F_5)Ti(NP(t\text{-}Bu)_3)Me_2$ with no detectable amounts of by-product.

Polymers 12-22

Polymers 12-22 were made according to the described polymerisation procedure on lab scale using catalyst B.

Polymers 11- 19

Polymers 11-19 were prepared using MMAO7 (modified methyl aluminoxane purchased from Akzo-Nobel, with typical Al content of 7wt% in Isopar E and 2,6-di-tert-butyl-4-methylphenol (BHT).

Polymers 20-21

Polymers were prepared using trytilium tetrakis(perfluorophenyl) borate (TBF20) in combination with MMAO-7/BHT.

Polymer 22

Polymer 22 was prepared using = trytilium tetrakis(perfluorophenyl) borate (TBF20) in combination with tri-isobutyl aluminium (TIBA).

Synthesis of $Me_5CpTiCl_2(NC(2,6\text{-}F_2Ph)(^iPr_2N)$; catalyst B

$Me_5CpTiCl_3$ (7.24g, 25 mmol) and N,N-diisopropyl-2,6-difluorobenzamidine (6.05g, 25.2 mmol) were dissolved in toluene (150 mL). Next, triethylamine (4.0 mL, 2.9 g, 29 mmol) was added and the reaction mixture was stirred for 18 hours. The reaction mixture was filtered and the residue was rinsed once with toluene (60 mL). The solvent of the combined organic phases was removed in vacuo. The residue was triturated with hexane (60 mL) once resulting in 12.18 g (99%) orange powder ($Me_5CpTiCl_2(NC(2,6\text{-}F_2Ph)(^iPr_2N)$).

A solution of methylmagnesiumbromide (16.5 mL, 3.0M solution in diethylether, 49.5 mmol) was added to a solution of $Me_5CpTiCl_2(NC(2,6\text{-}F_2Ph)(^iPr_2N)$ (12.18g, 24.7mmol) in toluene (100 mL) at -78°C. The reaction mixture was stirred at room temperature for 18 hours. The reaction mixture was filtered and the solvent from

the filtrate was removed in vacuo. The residue was triturated with hexane (100mL) resulting in 10.9 g of pure product as a yellow powder of $Me_5CpTiCl_2$(NC(2,6-F_2Ph)($^iPr_2$N) (97%).

Polymer 23

Polymer 23 was made on lab scale with a "Constrained Geometry Catalyst" (Catalyst C) Me2SiC5Me4(N-t-Bu)TiMe2., purchased from Degussa. Tri-octylaluminum (TOA) was used as scavenger and TBF20 as activator.

Polymer 24

Polymer 24 is a commercial grade, purchased from Exxon.

Polymers 25-28

Polymers 25 through 28 are commercial grades purchased from Mitsui (polymer 25) and Sumitomo (polymers 26 – 28).

Polymerisation procedure on lab scale

The polymerisation was carried out in a solution polymerisation reactor with a volume of 3L. The feed streams were purified by contacting with various absorption media to remove catalyst-killing impurities such as water, oxygen and polar compounds as is known to those skilled in the art.

The process is continuous in all feed streams. Premixed hexane (C6), propene, ethylene, dienes (5-ethylidene-2-norbornene (ENB), 5-vinyl-2-norbornene (VNB), 1,9-decadiene and/or norbornadiene (NBND) , hydrogen, were precooled before being fed to the reactor.

The catalyst components were dosed to the reactor as solutions in hexane, except for T-BF20, which was dosed as a solution in toluene.

The olefinic elastomer solution was continuously removed through a discharge line where a solution of Irganox-1076 in iso-propanol was added and subsequently worked-up by continuously steam stripping. EPDM was obtained after batch wise drying of the olefinic elastomer on a mill. The olefinic elastomers were analyzed amongst other methods by using FT-IR for composition, Mooney viscosity (ML(1+4) 125°C) and SEC-DV for the molecular weight and molecular weight distribution.

Table 1: The dilution slope (S_b) and $\Delta\delta$ for a series of different elastomers.

number	polymer	cat	activator	ML	C2 wt%	third mon.	wt% third mon.	Dd	S_b
1	K520	Z-N	SEAC	46 (125°C)	58	DCPD	4.5	8	26
2	K4802	Z-N	SEAC	77 (125°C)	52	ENB	4.3	27	15
3	K820	Z-N	SEAC	74 (125°C)	58	DCPD	4.5	4	28
4	K8340A	Z-N	SEAC	80 (125°C)	55	ENB	5.5	9	28
5	K7506	Z-N	SEAC	70 (125°C)	57	ENB	4.5	16	29
6	K5508	Z-N	SEAC	55 (125°C)	70	ENB	4.6	21	22
7	K39F	Z-N	SEAC	54(150°C)	52.5	ENB	9	17	24
8	K27	Z-N	SEAC	70 (125°C)	54	ENB	5	20	19
9	05173b	Z-N	SEAC	82 (125°C)	56.5	VNB	3.3	1	28
10	K6622A	Z-N	SEAC	67 (125°C)	68	ENB	2.4	12	22
11	04289a	A	MAO	124(125°C)	55	VNB	1.8	11	60
12	05018a	B	MAO	87(125°C)	49.2	VNB	2.7	16	34
13	05401A	B	MAO	87(125°C)	48.6	VNB	3.5	8	45
14	05111a	B	MAO	69 (125°C)	65.6	VNB	0.45	33	19
15	04564b	B	MAO	66 (125°C)	65.1	VNB	1.7	12	32
16	05122b	B	MAO	53(125°C)	70	VNB	3.2	2	37
17	05088a	B	MAO	76(125°C)	47.8	NBND	0.2 (+0.4w% VNB)	15	20
18	05113c	B	MAO	70 (125°C)	63.2	NBND	0.15	12	30
19	05155c	B	MAO	79(125°C)	52	1,9-decadiene	0.4 (+1w% VNB)	16	20
20	04570c	B	T-BF	67 (125°C)	65.7	VNB	0.4	12	27
21	05083a	B	T-BF	79(125°C)	49.8	VNB	0.5	11	29
22	05333a	B	T-BF	54(125°C)	68.9	VNB	0.2	20	21
23	05003A	CGC	T-BF	68 (125°C)	64.2	ENB	2.7	14	21
24	Vistalon 7500	Z-N	Al-alkyl	91 (125°C)	52.3	ENB	5.7	12	27
25	EPT4045	Z-N	Al-alkyl	45 (100°C)	53.4	ENB	7.6	16	16
26	ESPRENE 505A	Z-N	Al-alkyl	47 (100°C)	45.3	ENB	9.5	10	19
27	ESPRENE 501A	Z-N	Al-alkyl	44 (100°C)	49.9	ENB	4	15	19
28	ESPRENE 505	Z-N	Al-alkyl	59 (125°C)	45	ENB	10	10	28

Determination of amount of gel particles

A fixed amount of EPDM polymer, in this case 10 grams, is mixed with an excess of white spirit (i.e. 500 ml). This mixture is stirred with a magnetic stirrer and held at 50°C for three days. Possible gel particles are removed by passing the

mixture through two types of filters. The first one having a pore size of 1 mm, while the pore size of the second one is 100 μm. The extract is then placed under vacuum at 80°C for three days. The weight of the thus obtained residue divided by the initial amount of polymer is taken as measure for the weight percent of gel particles, present in the polymer.

The amount of gel particles was measured in polymer 9 and in polymer 16. Both polymers have the same approximate Δδ-value and VNB percentages (see table 1). The result is given in table 2.

Table 2: Amount of gel particles

Polymer	Weight % gel particles
9	9.4
16	0.05

These results demonstrate that polymers suitable for the compounds according to the invention, have a substantially lower level of gel particles than polymers with an equal amounts of third monomer, but with a dilution slope S_b of less than 30.

Example 1 and comparative Experiments A and B

Polymers 12, 13, 15 and 16 are examples of suitable olefinic elastomers for the compounds according to the invention. While the other elastomers, denoted in Table 1, serve as olefinic elastomers in comparative examples.

Preparation of the compounds

In order to illustrate the effect of the dilution slope of the elastomer on the resulting extrusion behaviour of a compound, three different elastomers were selected, namely from polymers 2 (K4802; S_b = 15), 5 (K7506, S_b = 29) and polymer 12 (05018a; S_b = 34). The first two polymers (2 and 5) are used for comparative experiments A and B, while polymer 12 is used for Example 1. For each of these elastomers a compound with a compound loading of 250 phr was prepared according to a composition as given in Table 3.

Table 3

Ingredient	phr	comment
Polymer	100	
N-550	88	carbon black
Sunpar 2280	52	processing oil
ZnO	5	activator for sulfur cure
Stearic Acid	1	processing aid
CaO	4	drying agent
Total phr	250	

Determination of extrusion stability and surface distortions

The extrusion stability of a compound was assessed by means of a piston velocity-controlled capillary rheometer (Rheograph 6000, Göttfert – software: Winrheo version 3.5). All experiments were done at 70°C using a capillary die with a length of 10 mm, a diameter of 2 mm and an entrance angle of 60°. The diameter of the reservoir is 12 mm.

In order to homogenize the temperature of the EPDM compound, the material is allowed to rest for 15 minutes after it is loaded into the reservoir. After this period, a constant piston velocity is applied until a steady state pressure is measured. The steady state pressure is defined by the software as the value of the pressure at which further variations in pressure are smaller than 1% after a specific time step. This time step is defined as $10/v_p+2$ seconds, where v_p is the applied piston velocity in mm/s. The throughput in the steady state is calculated as $\pi d^2 v_p/4$, wherein d is the diameter of the die. At the steady state condition a piece of extrudate is collected. This procedure is repeated for different, increasing values of the piston velocity. The acquired extrudates are allowed to relax at room temperature during 1 hour, after which micrograph pictures of the relaxed extrudates were taken with a video microscope (microviper).

Results

Optical micrographs of the extrudates of respectively comparative examples K4802 and K7506 and Example 1 (polymer nr 12) taken from extrudates at different throughputs were scanned. With a computer program the width of the extrudate was determined over a length of 20 mm. From these date the Roughness of the extrudate was calculated as R_q/d, wherein R_q is the average deviation A from the

average extrudate diameter D, extruded from a die with a diameter d as illustrated in Figure 1. The results are given in Figure 2 for K4802 (♦), K7506 (■) and polymer nr 12 (▲).

Conclusion extrudates surface

Fig. 2 shows the Roughness versus the throughput of the extrudate. This Figure clearly demonstrate that the compound of this invention displays significantly less extrudate distortions at high throughput, compared to the distortions of the extrudates of the Comparative Examples A and B. The compound according to the invention remained stable even at a throughput of 213 cm^3/min.(fig 3(c)).

Examples 2 - 4 and Comparative example C

Determination of compression set:

The compression set is measured in accordance with ISO 188 type B .at 180°C

Results

The compound recipes for examples 2- 4, containing a blend of polymers 12 and 16, and for comparative example C (blend of polymers 3 and 4) are shown in Table 4. Examples 2 - 4 contain different amounts of peroxide (Perkadox 14-40 MB).

Table 4: Compound recipes for assessment of curing behaviour

Description	Example 2	Example 3	Example 4	Example C
Descr.	**4.5phr Peroxide**	**3.6phr Peroxide**	**2.7phr Peroxide**	**ZN Reference 4.5phr Peroxide**
Polymer 12	60.00	60.00	60.00	
Polymer 16	68.00	68.00	68.00	
Polymer 4				60.00
Polymer 3				68.00
Whiting Omya BSH				
Carbon black N-550	75.00	75.00	75.00	75.00
Carbon black N-772				
Par.oil Flexon 876				
Struktol WB 212				
TMQ (A. Resin D)	1.00	1.00	1.00	1.00
Perkadox 14-40 MB	**4.50**	**3.60**	**2.7**	**4.50**
TAC-70				
PEG	4.00	4.00	4.00	4.00
MgO (M. DE)	4.00	4.00	4.00	4.00
Carbon black Dur O	20.00	20.00	20.00	20.00
Al-silicate S. N85	15.00	15.00	15.00	15.00
Tudalen B-8014	7.00	7.00	7.00	7.00
EDMA-70 (R.EDMA)	2.00	2.00	2.00	2.00
DHBP-40 (T. 101)	3.50	2.80	2.80	3.50
Protektor G3108	1.50	1.50	1.50	1.50
Total phr	**265.50**	**263.90**	**263.90**	**265.50**

Table 5: Compression set data for four different compounds

Description	Example 2	Example 3	Example 4	Example C
Descr.	**4.5phr Peroxide**	**3.6phr Peroxide**	**2.7phr Peroxide**	**ZN Reference 4.5phr Peroxide**
Test time [h]	22	22	22	22
Test temp. [°C]	160	160	160	160
Results				
Set 5 sec [%]	**32**	**38**	**49**	**40**
Set 60 min [%]	**27**	**31**	**37**	**33**
Test time [h]	22	22	22	22
Test temp. [°C]	70	70	70	70
Results				
Set 5 sec [%]	**14**	**16**	**29**	**21**
Set 60 min [%]	**10**	**12**	**18**	**15**

The result from the compression set experiments, done both at 70°C and 160°C, are shown in Table 5. As can be observed in this table, the compression set results at equal amounts of peroxide are significantly lower and hence better for example 2 than for the comparative example C. Furthermore, this table demonstrates that the compounds according to this invention, despite lower levels of peroxide (e.g. example 3), can even exceed the compression set performance of other compounds (comparative example C).

Example 5 and Comparative Example D

Extrusion experiments

In this Example a compound according to the invention based on polymer 12, available as DE6002™ (similar to 05018a) was compared with a compound based on K8340A™, both commercial products of Koninklijke DSM N.V. (Netherlands) in a low filled wiper blade composition given in Table 6.

Table 6

Experiment/Comp. example	5	D
EPDM DE 6002		100
EPDM KELTAN 8340A	100	
ZnO-active	4	4
Stearic acid	0.7	0.7
CaO-80 (K. GR/DAB)	8	8
Carbon black N-550	105	105
Carbon black N-990	40	40
N-Oil Nyflex 222b	40	40
Total phr	297.7	297.7

The Moony of these compounds according ISO 289 at 100 and 125 °C are given in Table 7.

Table 7

Experiment		5	D
Test temp.	[°C]	100	100
Initial	[MU]	167.2	175.4
ML	[MU]	132.21	121.49
Slope	[IM/Is]	0.4654	0.5065
Test temp.	[°C]	125	125
Initial	[MU]	133.9	131.6
ML	[MU]	93.90	84.72
Slope	[IM/Is]	0.5038	0.4947

Table 8 shows the results of the Garvey die test according to ASTM 2230.

Table 8

Experiment		5	D
Speed	[rpm]	30	30
Output	[gr/mi]	206	208
Die swell	[%]	28	19
* Swelling		4	4
* 30° Edge		4	4
* Surface		4	4
* Corners		3	4
Speed	[rpm]	50	50
Output	[gr/mi]	308	374
Die swell	[%]	41	41
* Swelling		3	3
* 30° Edge		4	4
* Surface		4	4
* Corners		3	4
Speed	[rpm]	70	70
Output	[gr/mi]	426	490
Die swell	[%]	32	28
* Swelling		4	4
* 30° Edge		4	4
* Surface		4	4
* Corners		2	4
Speed	[rpm]	90	90
Output	[gr/mi]	538	785
Die swell	[%]	38	37
* Swelling		4	4
* 30° Edge		2	4
* Surface		3	4
* Corners		1	4

At a screw speed of 30 rpm the K8340 compound already displayed instabilities at the sharpest angle, while the compound according to the invention did not showed any instabilities even up to screw speeds of 90 rpm, which is the maximum rpm of the extruder).

Comparative Experiments E – J

Example 1 and Comparative experiments A and B were repeated, but now with a compound composition as given in Table 9 (Comparative experiments E, F and G) and with the unfilled polymers DE 6002, K4802 and K7506 respectively (Comparative experiments H, I and J).

Table 9

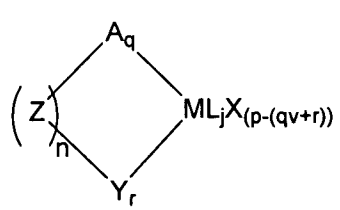
Ingredient	phr
Polymer	100
N-550	215
Sunpar 2280	125
ZnO	5
Stearic Acid	1
CaO	4
Total	450

The results are given in Figure 3 for K4802 unfilled(♦), K7506 unfilled(■) and DE6002 unfilled (▲) and for K4802 450 phr(◊), K7506 450 phr (□) and DE6002 450 phr (Δ).

This figure shows that the polymer has no influence on the processing properties for compound loadings of 450 phr. Figure 3 further demonstrates that unloaded rubber can hardly be processed at all.

CLAIMS

1. An elastomeric compound comprising at least one olefinic elastomer comprising ethylene, an α-olefin, from 1 to 7 wt% vinyl norbornene and from 0 to 15 wt% of a second non-conjugated polyene, wherein the wt% are related to the total weight of ethylene, α-olefin, vinyl norbornene and the second non-conjugated polyene, and which elastomer has long chain branching corresponding with $\Delta\delta$ <20, wherein $\Delta\delta$, expressed in degrees, is calculated from the difference between the phase angle δ between stress and strain in a dynamic shear measurement at 125°C at a frequency of 0.1 rad/s and the phase angle δ at a frequency of 100 rad/s, the compound further comprising a solid filler and an oil, such that the compound has a compound loading between 120 and 300 phr, characterized in that the said olefinic elastomer satisfies the following relation $S_b > 30$, wherein S_b is the slope in a graph of $\ln(a_c)$ versus Φ, in which a_c is the factor along which the low frequency part (ω < 1 rad/s) of the phase angle δ versus ω plots, measured at at least one volume fraction Φ between 0.2 and 1 of the olefinic elastomer in squalane, must be shifted to coincide with a δ versus ω plot of an undiluted polymer (Φ =1), and wherein the δ versus ω plots results from a frequency sweep performed on a stress controlled rheometer carried out at 125 °C under nitrogen atmosphere, using a parallel plate geometry in shear.
2. Compound according to claim1 wherein the olefinic elastomer has a ML(1+4)125°C according to ASTM D-1646 in the range of from 30 to 130 MU.
3. Method for the preparation of a compound according to claim 1, by mixing 100 phr elastomeric polymer with between 20 and 200 phr of a solid filler, an oil and other compounding ingredients, characterized in that the elastomeric polymer is prepared by polymerising at least ethylene, an alpha-olefin and vinyl norbornene in the presence of a catalyst system comprising:
a metal-organic compound of the following formula:



(formula 1)

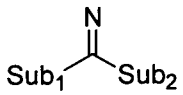
where:

M is a metal of group 3 –13 or the lanthanide series, and p is the valency of the metal M;

A represents a neutral or anionic spectator ligand whose valency v is 0,1 or 2, and q is an integer denoting the number of spectator ligands A;

Z is an optional bridging moiety, and n is the integer number of parallel bridging moieties Z;

Y is an amidine-containing spectator ligand represented by formula 2:



(formula 2),

wherein the amidine-containing ligand is covalently bonded to the metal M via the imine nitrogen atom, Sub_1 is a substituent, which comprises a group 14 atom through which Sub_1 is bonded to the imine carbon atom. Sub_2 is a substituent, which comprises a heteroatom of group 15-16, through which Sub_2 is bonded to the imine carbon atom;

r is an integer > 0;

L is an optional neutral Lewis basic ligand, and j is an integer denoting the number of neutral ligands L, and

X is an anionic ligand that may be independently selected from the group consisting of hydride, halide, alkyl, silyl, germyl, aryl, amide, aryloxy, alkoxy, phosphide, sulfide, acyl, pseudo halides such as cyanide, azide, and acetylacetonate, or a combination thereof.

and a cocatalyst comprising an aluminoxane.

4. Extruded part comprising a cured compound according to claim 1 or 2.

FIGURE 1/3

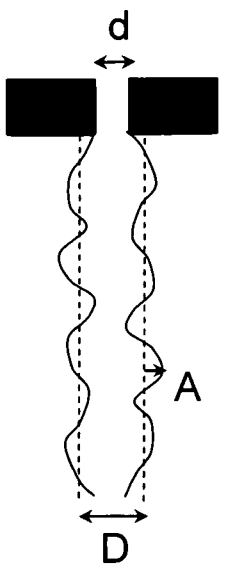


FIGURE 2/3

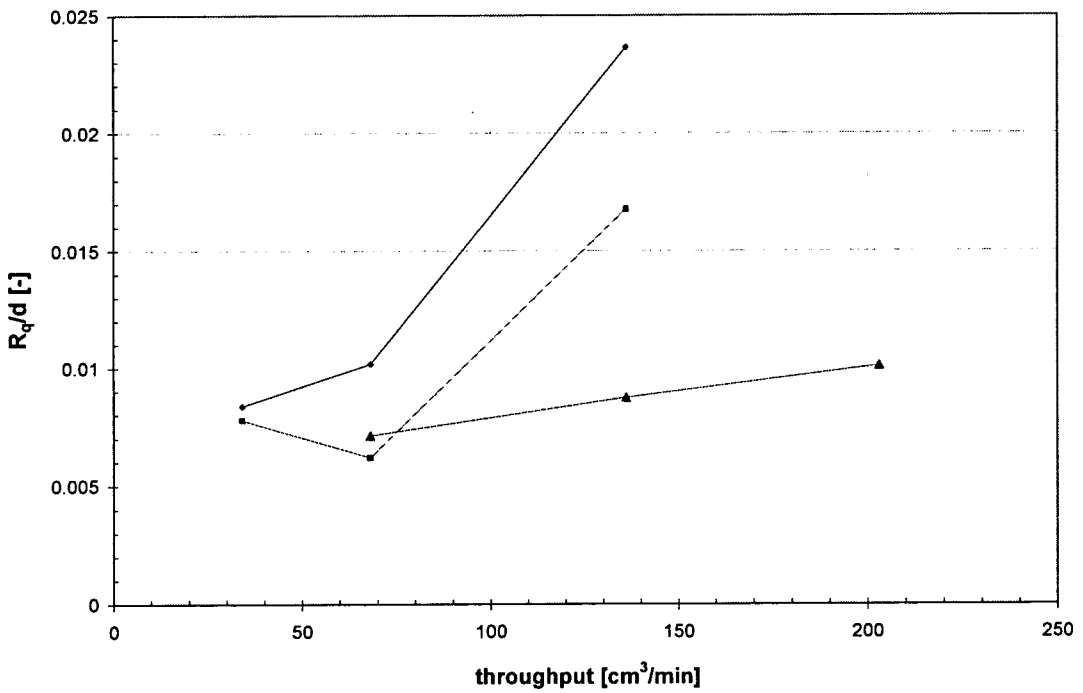
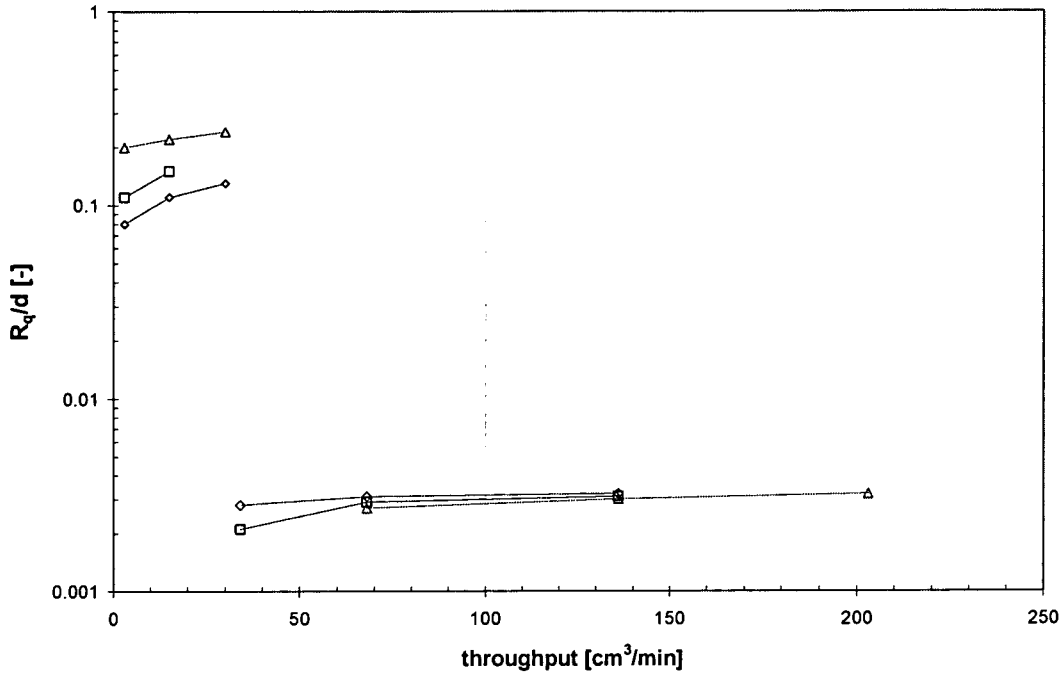


FIGURE 3/3



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2008/000903

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08F210/18 C08L23/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08F C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
27 March 2008	04/04/2008

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Lippert, Sigrid

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2008/000903

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2008/000903

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