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(54) Title: PROCESS FOR PRODUCING ARTICLES FROM ETHYLENE POLYMER WITH AN INTRINSIC VISCOSITY OF AT LEAST 4 DL/G		
(57) Abstract <p>The invention relates to a process for producing articles from ethylene polymer with an intrinsic viscosity (IV) of at least 4 dl/g measured in decalin at 135 °C, with a low density of entanglement, starting from a composition comprising the ethylene polymer and an auxiliary, which composition is pressed through an opening below the melting point of the ethylene polymer, which auxiliary is a non-solvent for the ethylene polymer capable of being formed into a paste with the ethylene polymer. The invention also relates to a paste comprising a composition of an ethylene polymer with an intrinsic viscosity (IV) of at least 4 dl/g, with a low density of entanglement and up to 50 % (vol.) non-solvent for the ethylene polymer.</p>		

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⁺ Any designation of "SU" has effect in the Russian Federation. It is not yet known whether any such designation has effect in other States of the former Soviet Union.

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PROCESS FOR PRODUCING ARTICLES FROM ETHYLENE POLYMER
WITH AN INTRINSIC VISCOSITY OF AT LEAST 4 DL/G

The invention relates to a process for producing articles from ethylene polymer with an intrinsic viscosity (IV) of at least 4 dl/g and with a low density of entanglement, starting from a composition comprising the ethylene polymer and an auxiliary, which composition is pressed through an opening below the melting point of the ethylene polymer.

Such a process is known from EP-A-292074. In that patent publication auxiliaries are used having a dissolving or swelling effect for the ethylene polymer at a temperature at which the mixture of ethylene polymer and auxiliary is processed. The disadvantage of these auxiliaries is that they are so expensive and/or so harmful to the environment that it is necessary for these substances to be recovered in a certain process step. This recovery involves a high amount of costs.

The object of the invention is to provide a process described in the opening lines that does not have said disadvantages, or to a less degree.

This object is achieved according to the invention in that the auxiliary is a non-solvent for the ethylene polymer capable of being formed into a paste with the ethylene polymer.

Surprisingly, it has been found that in the process according to the invention non-solvents too, once they are mixed with the ethylene polymer, are capable of realizing a cohesion between the polymer particles during the pressing operation carried out below the melting point of the pure ethylene polymer. This cohesion has been found to be so

strong that articles are formed that are suited as such to
serve as intermediate products for the production of
5 articles with a high tensile strength and a high modulus.

Suitable non-solvents according to the invention
are those auxiliaries in which the ethylene polymer does not
appreciably swell or dissolve at the processing temperature.
The non-solvent according to the invention must have a
10 melting point below the melting point of the ethylene
polymer. By heating a vessel containing the auxiliary and
particles of high molecular weight ethylene polymer to the
processing temperature and observing the swelling and
dissolution behaviour of the ethylene polymer particles, it
15 is possible to easily determine by experiment what
auxiliaries are suited for the invention. If there is no
appreciable swelling or dissolution, the auxiliary is a
non-solvent according to the invention. Examples of suitable
non-solvents are water and alcohols, for instance methanol,
20 n-propanol, isopropanol, ethanol and n-butanol. Highly
suitable as non-solvent is water. This has the advantage
that it is cheap and environmentally benign. Butanol has the
advantage that it is cheap and that it is easier to remove
from the moulded article than water.

25 Preferably a surface tension reductant is added to
the non-solvent. To this end the surface tension reductants
known in the art can be used, such as anionic, kationic and
non-ionic detergents. A suitable surface tension reductant
is, for instance, the detergent TritonR N 101 of Rohm &
30 Haas. The said surface tension reductant is added to the
non-solvent in, for instance, a concentration of 1% (wt).
The amount of surface tension reductant must be such that
the ethylene polymer particles are so wetted by the
non-solvent that a homogeneous paste can be formed. After
35 the formation of the paste, the surface tension reductant
can be removed from the ethylene polymer, for instance by
washing. After removal, the concentration of surface tension
reductant in the ethylene polymer is preferably less than
0.05% (wt), more particularly less than 0.01% (wt),

calculated on the ethylene polymer.

The concentration of the non-solvent in the
5 composition is preferably not above 50% (vol.) calculated on
the composition. Higher concentrations, though possible,
usually result in a paste that can be less readily pressed.
Specifically, the concentration amounts to 10-40%.

Ethylene polymer with a low density of entanglement
10 is known from, for instance, US-A-4769433. In it the drawing
is described of never previously dissolved or melted
ultra-high molecular weight polyethylene ('virgin PE')
prepared by polymerization at relatively low temperatures.
Such ethylene polymers with a low density of entanglement
15 can be drawn well below the melting point of the ethylene
polymer. In this specification, therefore, an ethylene
polymer with a low density of entanglement is defined as an
ethylene polymer with a maximum draw ratio of at least 20.

The maximum draw ratio is determined as follows. A
20 layer of ethylene polymer powder having a thickness of 2 mm
is compressed in a round mould with a diameter of 5 cm for 5
minutes at room temperature under a weight of 50,000 kg. The
resulting round film is subsequently compressed in a flat
mould for 10 minutes at 130°C under a weight of 100,000 kg.
25 From the resulting film a dumb-bell test specimen is punched
having a length of 10 mm between the shoulders and a width
of 2 mm. At a temperature of 130°C, this test specimen is
drawn in a Zwick 1445 tensile tester at a speed of 10 mm/min
until the specimen breaks. The maximum draw ratio is
30 determined as the quotient of the length of the part of the
specimen between the shoulders at the moment when the test
specimen breaks and the length thereof before the drawing
(10 mm).

The maximum draw ratio of the ethylene polymer is
35 at least 20, preferably at least 40 and specifically at
least 80.

The 'virgin' ethylene polymer as prepared according
to US-A-4769433 can further be characterized by the
difference between the initial melting enthalpy of a sample

and the melting enthalpy that is obtained when the sample has melted completely and has subsequently solidified again. The difference (fall) in melting enthalpies is preferably at least 10% of the initial melting enthalpy, specifically at least 20%. Moreover, the crystallinity of the ethylene polymer just mentioned is high, at least 75%. Although the above applies to the ethylene polymers according to US-A-4769433, ethylene polymers with a low density of entanglement need not always comply with the above criteria of crystallinity and difference in melting enthalpies.

Melting temperatures T_m and melting enthalpies ΔH can be determined with differential scanning calorimetry (DSC) at a scanning speed of 5°C/min and a commencing temperature of 40°C. The DSC measurements in the experiments have been carried out with a Perkin Elmer DSC-7 on samples weighing $4 \cdot 10^{-3}$ g. Calibration of the DSC measurements was effected with indium ($T_m = 156^\circ\text{C}$ and $\Delta H = 28.45$ J/g). The melting enthalpy ΔH is determined from the area below the melting curve. Crystallinities (%) are calculated by dividing the melting enthalpy ΔH of the sample by the melting enthalpy of 100% crystalline polymer. The ΔH for 100% crystalline polymer is assumed for polyethylene to amount to 293 kJ/kg.

The ethylene polymer according to the invention consists of a homo or copolymer of ethylene with a DSC crystallinity of at least 30%. Preferably the DSC crystallinity is at least 50%.

The intrinsic viscosity (IV) of an ethylene polymer according to the invention measured in decalin at 135°C is at least 4 dl/g, specifically at least 6 dl/g, more specifically it amounts to 8-40 dl/g.

In the process according to the invention preference is given to the use of linear ultra-high molecular weight polyethylene (UHMWPE). By UHMWPE is meant herein linear polyethylene having fewer than 10 side chains per 1000 carbon atoms and preferably having fewer than 3 side chains per 1000 carbon atoms, or such a polyethylene as

contains also minor amounts, preferably less than 5 moles %, of one or more other alkenes copolymerized with it, such as
5 propylene, butylene, pentene, hexene, 4-methyl-pentene, octene, etc., which polyethylene or copolymer of ethylene has an intrinsic viscosity of at least 5 dl/g. The polyethylene may further contain minor amounts, preferably 25% (wt) at most, of one or more other polymers,
10 specifically an alkene-1-polymer, such as polypropylene, polybutadiene or a copolymer of propylene with a minor amount of ethylene.

Such an UHMWPE can be made, for instance, by applying a Ziegler or a Phillips process using suitable
15 catalysts and under polymerization conditions known in the art.

The ethylene polymer may also contain non-polymeric materials, such as waxes and fillers. The amount of these materials may be up to 60% (vol.) calculated on the ethylene
20 polymer.

The pressing of the paste through an opening may be done by the methods known in the art, for instance by calandring or by means of an extruder, such as a ram extruder or a screw extruder.

25 Preference is given to the extruders, because in these it is possible to press the paste through a channel-shaped opening, which is an advantage for realizing an orientation of the ethylene polymer chains into the direction in which the material is pressed. Such orientation
30 is promoted particularly by using an extrusion channel whose cross section decreases into the direction into which the material is pressed. The fact is that the cohesion of the moulded article or of the extrudate increases as the orientation of the ethylene polymer chains increases. Owing
35 to the increased cohesion of the ethylene polymer in the moulded article or in the extrudate, the manageability is increased, which is an advantage for any further treatment.

The ratio between the areas of the cross sections at the beginning (A_0) and at the end (A_1) of the pressure

channel is referred to as the reduction ratio (RR), which, with channels with a round cross section, equals the square
5 of the ratio of the diameters $(D_0/D_1)^2$ at respectively the beginning (D_0) and the end (D_1) of the pressure channel.

Though a RR of 100 or higher is possible, preference is given to the use of a RR lower than 60, even more preference to the use of a RR lower than 50, for
10 obtaining a homogeneous continuous extrudate.

A further measure for obtaining an increased cohesion of the ethylene polymer in the moulded article or in the extrudate is that the the paste is pressed through an opening at a processing temperature of between 80 and 120°C,
15 preferably between 90 and 120°C. A major advantage of pressing the paste in this temperature range is that the moulded article or the extrudate is better qualified for an after-treatment consisting in the drawing of the moulded article or the extrudate to obtain a higher tensile strength
20 and E-modulus in the direction of drawing. This treatment is highly advantageous if from the moulded article or from the extrudate filaments, tapes or films are produced that must have a high tensile strength and modulus.

It is an advantage in obtaining filaments, tapes or
25 films with a high tensile strength and modulus if, after removal of the auxiliary material, the moulded article or the extrudate is subjected, before the drawing, to a short pressure treatment between 50 and 120 MPa at a temperature of between 80 and 120°C, because it has been found that the
30 drawing can then be carried out with fewer breaks at a particular draw ratio. This pressure treatment can be carried out in any manner known in the art, for instance by rolling.

The invention is further elucidated below with
35 reference to an embodiment.

Example I

UHMWPE with an IV of 29 dl/g measured in decalin at 135°C was obtained by polymerizing ethylene at a temperature

of -7°C in the presence of a Ziegler catalyst as in
US-A-4769433. The resulting UHMWPE has a maximum draw ratio
5 of 100. It has a melting point of 141°C measured according
to a standard DSC method (highest peak in the DSC diagram)
and a melting enthalpy of 237 J/g . The melting enthalpy of
the sample of the same ethylene polymer, melted only once
and then solidified, measured according to the same standard
10 DSC method is 30% lower. The X-ray crystallinity is 81%.

The ethylene polymer was mixed in the form of a
powder with demineralized water to which 1% (wt) Triton[®] N
101 (nonylphenol-polyethylene oxide) of Rohm & Haas had been
added as surface tension reductant. The mixing temperature
15 was 25°C . The concentration of the water in the paste
obtained by the mixing was 39% (vol.). The paste was placed
in an Instron rheograph the plunger of which is provided
with a pressure recorder. The capillary of the rheograph has
a reduction ratio of 16. The half vertex angle of the
20 capillary is $9^{\circ}20'$. The round entrance aperture of the
capillary has a diameter of 9.6 mm. After venting the paste
and after a temperature stabilization at 115°C for 10 min.,
the plunger was moved at a speed of 0.2 cm/min . and the
paste was pressed through the capillary and left the device
25 in the form of a moulded article or extrudate.

The stabilization and pressing temperature was
 115°C and the pressure observed during the pressing
operation was 55 MPa. After conditioning for 15 minutes at
 110°C , the extrudate was drawn at 120°C with a length of 21
30 mm between the clamps of an Instron drawing device and a
drawing speed of 10 mm/min .

After that the tensile strength and the modulus
were measured, which were 1.5 GPa and 70 GPa respectively.

When, after evaporation of the water, the
35 extrudates were first, for a short time, subjected to a
pressure of 100 MPa at a temperature of 110°C and were
subsequently drawn, the measured tensile strength and
modulus were respectively 2.1 GPa and 98 GPa with an
elongation at break of 2.2%.

Comparative Experiment A

In this experiment the ethylene polymer used was
5 UHMWPE of the HIFAX[®] 1900 type of the firm of Hercules. This
ethylene polymer has an IV of 29 dl/g measured in decalin at
135°C and a maximum draw ratio of 16. It has a melting point
measured according to a standard DSC (highest peak in the
DSC diagram) of 142°C and a melting enthalpy of 240 J/g. The
10 melting enthalpy of the sample of the same ethylene polymer,
melted once and subsequently solidified, measured according
to the same standard DSC method is 30% lower. The X-ray
crystallinity is 82%.

As in experiment I, the ethylene polymer was mixed
15 in the form of a powder with demineralized water to which 1%
(wt) Triton[®] N 101 had been added. The concentration of the
non-solvent in the paste obtained by the mixing was 39%
(vol.). The paste was extruded as in experiment I.

The stabilization and pressing temperature was
20 115°C and the pressure observed during the pressing
operation was about 55 MPa. The extrudate was conditioned
and drawn as in experiment I.
The drawability of the extrudate was found to be poor, even
after pressure treatment as in example I, and no homogeneous
25 product could be formed by drawing.

C L A I M S

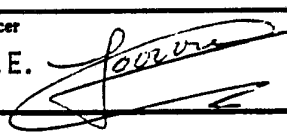
- 5 1. Process for producing articles from ethylene polymer
with an intrinsic viscosity (IV) of at least 4 dl/g and
with a low density of entanglement, starting from a
composition comprising the ethylene polymer and an
auxiliary, which composition is pressed through an
10 opening below the melting point of the ethylene polymer,
characterized in that the auxiliary is a non-solvent for
the ethylene polymer capable of being formed into a
paste with the ethylene polymer.
- 15 2. Process according to claim 1, characterized in that the
concentration of the auxiliary is up to 50% (vol.)
measured on the composition.
3. Process according to claim 1 or 2, characterized in that
the auxiliary is water which a surface tension reductant
has been added to.
- 20 4. Process according to claim 1 or 2, characterized in that
the auxiliary is n-butanol.
5. Process according to any one of claims 1-4,
characterized in that the opening is a channel whose
cross section decreases into the direction in which the
25 material is pressed.
6. Process according to any one of claims 1-5,
characterized in that the material is pressed through
the opening at a temperature of between 80 and 120°C.
7. Process according to claim 6, characterized in that the
30 material is pressed through the opening at a temperature
of between 90 and 120°C.
8. Process for producing filaments, tapes and films with a
high tensile strength and a high modulus, starting from
articles obtained according to any one of claims 1-7,
35 characterized in that the articles are first subjected
to a pressure of between 800 and 1500 bar at a
temperature of between 80 and 120°C and are subsequently
drawn at a temperature of between 120 and 140°C.

9. Paste comprising a composition of an ethylene polymer with an intrinsic viscosity (IV) of at least 4 dl/g, with a low density of entanglement and up to 50% (vol.) non-solvent for the ethylene polymer.
10. Process or paste as described in substance and/or obtained by means of examples.
11. Filament, tape or film obtainable by the process according to any of claims 1-8.

INTERNATIONAL SEARCH REPORT

PCT/NL 91/00150

International Application No

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int. Cl. 5	C08J3/05; D01F6/04	C08L23/06; C08K3/20; C08K5/05
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int. Cl. 5	C08J ; C08L ; C08K ; D01F	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category ^o	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	EP,A,0 176 350 (MITSUI PETROCHEMICAL) 2 April 1986 see page 6, line 8 - line 16; claims 1,2,11-13 ---	1-3,6-11
X	EP,A,0 173 456 (MITSUI PTROCHEMICAL) 5 March 1986 Abstract see page 11, line 3 - line 10; example 48 ---	1-3
A	EP,A,0 277 750 (MITSUI PETROCHEMICAL) 10 August 1988 see page 3, line 27 - line 39; claim 1 ---	1
<p>^o Special categories of cited documents :¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
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09 DECEMBER 1991	09. 01. 92	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	GOOVAERTS R. E. 	

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
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This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		US-A- 4808367	28-02-89
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