PRODUCTION OF POLYETHYLENE HAVING IMPACT RESISTANCE
HERSTELLUNG VON SCHLAGFESTEM POLYETHYLEN
PRODUCTION DE POLYETHYLENE RESISTANT AUX IMPACTS

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References cited:
EP-A- 0 000 751
US-A- 4 151 122
US-A- 4 405 768

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Description

[0001] The present invention relates to a process for producing polyethylene having impact resistance and to a catalyst for use in such a process.

[0002] Polyethylene is known for use in the manufacture of a wide variety of articles. The polyethylene polymerisation process can be varied in a number of respects to produce a wide variety of resultant polyethylene resins having different physical properties which render the various resins suitable for use in different applications. In particular, it is known to use polyethylene for use in applications where the polyethylene is required to have impact resistance. For example, polyethylene is known for use in the manufacture of pipes where it is obviously required that the material of the pipe has sufficient impact resistance so as to avoid inadvertent fracture in service. Furthermore, polyethylene is known for use as a film where the property of impact resistance of the film can be of importance.

[0003] Chromium-based catalysts used for the production of polyethylene have been known for some time. The catalysts may have been subjected to pre-treatment processes prior to the polymerisation reaction. The pre-treatment processes may include chemical reduction of the chromium to a lower valence state, e.g. by carbon monoxide. Such a process is disclosed in, for example, EP-A-0591968.

[0004] US-A-5208309 discloses a linear, very low density polyethylene polymerisation process. In the polymerisation process, a cocatalyst such as a boron alkyl, most particularly triethyl borane (TEB), is employed which tends to generate an in situ comonomer and thus depresses the density of the resultant polyethylene resin. The catalyst support is a silica-titania support and for producing a polymer with the most desirable characteristics it is preferred for the support to contain 5 to 8wt% titanium. The specification does not address the problem of the production of polyethylene having impact resistance.

[0005] US-A-4151122 discloses the reduction and reoxidation of a cogel or self-reduced catalyst in which oxidation of a catalyst is employed after reduction of a catalyst, such as by carbon monoxide, for boosting the melt index of the resultant polyethylene resin. There is no disclosure of a process for producing polyethylene having impact resistance.

[0006] US-A-4405768 discloses the addition of titanium to a catalyst for boosting the melt index of the polyethylene resin. Again, there is no disclosure of a process for producing polyethylene having impact resistance.


[0008] The present invention aims in one aspect to provide a process for producing polyethylene having improved impact resistance.

[0009] It is known in the art that the physical properties, in particular the mechanical properties, of a polyethylene product vary depending on what catalytic system was employed to make the polyethylene. This is because different catalyst systems tend to yield different molecular weight distributions in the polyethylene produced. Thus, for example, the properties of a polyethylene product produced using a chromium-based catalyst (i.e. a catalyst known in the art as an "Phillips catalyst") tend to be different from the properties of a polyethylene produced using a different catalyst, for example a Zeigler-Natta catalyst. The production of polyethylene using a chromium-based catalyst is desirable to enable the particular polyethylene product obtainable thereby to be manufactured.

[0010] In a second aspect the present invention aims to provide a process for producing polyethylene having impact resistance using a chromium-based catalyst.

[0011] Accordingly, the present invention provides a process for producing polyethylene having impact resistance, the process comprising polymerising ethylene, or copolymerising ethylene and an alpha-olefinic comonomer comprising from 3 to 10 carbon atoms, in the presence of a chemically reduced chromium-based catalyst containing in a support thereof from 2 to 3wt% of titanium, based on the weight of the catalyst, said polymerisation being carried out in the absence of a cocatalyst.

[0012] The present invention further provides a chromium-based catalyst for the production of polyethylene by polymerising ethylene or copolymerising ethylene and an alpha-olefinic comonomer comprising from 3 to 10 carbon atoms, the catalyst being chemically reduced and containing in a support from 2 to 3wt% of titanium, based on the weight of the catalyst.

[0013] The present invention is predicated on the surprising discovery by the present inventor that the chemical reduction, preferably by carbon monoxide, of a chromium-based catalyst containing from 2 to 3wt% titanium in its support can unexpectedly yield a polyethylene product having improved impact resistance.

[0014] The chromium-based catalyst preferably comprises a supported chromium oxide catalyst having a titania-containing support, for example a composite silica and titania support. A particularly preferred chromium-based catalyst may comprise from 0.5 to 5wt% chromium, preferably around 1wt% chromium, such as 0.9wt% chromium based on the weight of the chromium-containing catalyst. The support comprises 2 to 3wt% titanium, more preferably around 2.3wt% titanium, based on the weight of the chromium-containing catalyst. The chromium-based catalyst may have a specific surface area of from 200 to 700 m²/g, preferably from 400 to 550 m²/g and a volume porosity of greater than
A particularly preferred chromium-based catalyst for use in the present invention comprises a catalyst, ("catalyst 1") having an average pore radius of 190A, a pore volume of around 2.1cc/g, a specific surface area of around 510 m²/g and a chromium content of around 0.9wt% based on the weight of the chromium-containing catalyst. The support comprises a composite silica and titania support. The amount of titania in the support provides that the catalyst as a whole comprises around 2.3wt% titanium.

The catalyst may be subjected to an initial activation step in air at an elevated activation temperature. The activation temperature preferably ranges from 500 to 850°C, more preferably 600 to 750°C, and is most particularly around 635°C.

In the preferred polymerisation process of the present invention, the polymerisation or copolymerisation process is carried out in the liquid phase, the liquid comprising ethylene, and where required an alpha-olefinic comonomer comprising from 3 to 10 carbon atoms, in an inert diluent. The comonomer may be selected from 1-butene, 1-pentene, 1-hexene, 4-methyl 1-pentene, 1-heptene and 1-octene. The inert diluent is preferably isobutane. The polymerisation or copolymerisation process is typically carried out at a temperature of from 90 to 100°C, more preferably from 50 to 100°C, and at a pressure of 20 to 42 bars, more preferably at a minimum pressure of around 24 bars.

Typically, in the polymerisation process, the ethylene monomer comprises from 0.5 to 8% by weight, typically around 6% by weight, of the total weight of the ethylene in the inert diluent. Typically, in the copolymerisation process, the ethylene monomer comprises from 0.5 to 6% by weight and the comonomer comprises from 0.5 to 3% by weight, each based on the total weight of the ethylene monomer and comonomer in the inert diluent.

The carbon monoxide-reduced catalyst for use in the process of the invention is introduced into the polymerisation reactor. The alkyene monomer, and comonomer if present, are fed into the polymerisation reactor in the inert diluent and the polymerisation product of polyethylene is discharged from the reactor and separated from the diluent which can then be recycled.

In accordance with the preferred process of the invention, in order to achieve good impact resistance for the polyethylene, the process is performed in order to achieve high density in the polyethylene. Accordingly, the process is carried out in the absence of a cocatalyst such as triethyl borane (TEB) which would tend to depress the density, and thus lower the impact resistance. Preferably, the polyethylene has a density of from 0.940 to 0.950g/cc and a high load melt index (HLMI) for resins within that density range of from 5 to 12g/10min Preferably, the polyethylene resin has a shear response (SR) of less than 80.

The process of the present invention can provide polyethylene resins having improved impact resistance. In particular, when the polyethylene resins are used to manufacture films, which are produced by blowing or extrusion, the impact resistance of the film as measured by impact of a dart can be significantly improved as compared to the use of an equivalent catalyst which has not been subjected to carbon monoxide reduction. When the polyethylene resins are used to produce pipes, the impact resistance of the pipe under pressure can be greatly increased as compared to the impact resistance of an equivalent pipe employing a polyethylene resin prepared by a polymerisation process using substantially the same chromium-based catalyst but not subjected to carbon monoxide reduction.

Example 1

In Example 1, a polyethylene resin was produced by the polymerisation process of the present invention in which a carbon monoxide-reduced chromium-based catalyst was employed. The catalyst employed in Example 1 was the chromium-based catalyst identified as catalyst 1 above which had been activated in dry air at a temperature of around 635°C and then subjected to a dry carbon monoxide reduction at a temperature of 370°C. The catalyst had a pore volume of 2.1cc/g and a specific surface area of 510 m²/g. The catalyst comprised 0.9% Cr and 2.3% Ti, each based on the weight of the catalyst. In Example 1, a liquid comprising 6.4wt% ethylene, 0.6wt% 1-hexene and the balance isobutane as an inert diluent was fed into a polymerisation reaction zone at a pressure of 42 bars and at a polymerisation temperature of 95°C. The catalyst was also fed into the polymerisation reaction zone. The resultant polyethylene resin was separated from the diluent and following processing to form pellets, the physical properties of the resultant resin were measured. These are shown in Table 1.
As may be seen from Table 1, the resultant resin had a high load melt index (HLMI) of 8.5 g/10', the high load melt index having been determined using the procedures of ASTM D 1238 using a load of 21.6 kg at a temperature of 190 °C. The melt index (MI2) was similarly measured (using the same procedures, with a load of 2.16 kg at 190 °C) and the ratio HLM/MI2 was calculated to yield a value for the shear response (SR) of the polyethylene resin of Example 1 of 68. The density of the polyethylene resin was measured as 0.946 g/cc, as shown in Table 1.

The polyethylene resin was then formed into a pipe having a diameter of 110 mm. The pipe was then subjected to an impact resistance test at 0 °C by subjecting the pipe to internal pressurisation. This test known as the RCP 54

### TABLE 1

<table>
<thead>
<tr>
<th>CATALYST</th>
<th>CO REDUCED CATALYST 1</th>
<th>CATALYST 1</th>
<th>CO REDUCED CATALYST 2</th>
<th>CO REDUCED CATALYST 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore Volume (cc/g)</td>
<td>2.1</td>
<td>2.1</td>
<td>2.1</td>
<td>2.1</td>
</tr>
<tr>
<td>Surface Area (m²/g)</td>
<td>510</td>
<td>510</td>
<td>420</td>
<td>510</td>
</tr>
<tr>
<td>Wt% Cr</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
</tr>
<tr>
<td>Wt% Ti</td>
<td>2.3</td>
<td>2.3</td>
<td>1.45</td>
<td>5.0</td>
</tr>
<tr>
<td>Activation Temp. (°C)</td>
<td>635</td>
<td>635</td>
<td>635</td>
<td>600</td>
</tr>
<tr>
<td>CO Reduction Temp. (°C)</td>
<td>370</td>
<td>-</td>
<td>370</td>
<td>370</td>
</tr>
<tr>
<td>RESIN</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HLMI (g/10')</td>
<td>8.5</td>
<td>9.6</td>
<td>10.0</td>
<td>8.0</td>
</tr>
<tr>
<td>SR</td>
<td>68</td>
<td>90</td>
<td>101</td>
<td>90</td>
</tr>
<tr>
<td>Density (g/cc)</td>
<td>0.946</td>
<td>0.946</td>
<td>0.947</td>
<td>0.947</td>
</tr>
<tr>
<td>PIPE APPLICATION</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pc S4/0°C (bar)</td>
<td>&gt;12</td>
<td>2.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>110 mm Diameter</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FILM APPLICATION</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Impact Resistance dart (g)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10µm</td>
<td>131</td>
<td>80</td>
<td>&lt;30</td>
<td>63</td>
</tr>
<tr>
<td>20µm</td>
<td>155</td>
<td>-</td>
<td>47</td>
<td>87</td>
</tr>
</tbody>
</table>
test, was in accordance with ISO/DIS 13477 or EN33477. It will be seen from Table 1 that the pipe failed at an internal
pressurisation of greater than 12 bars.

Comparative Example 1

Table 1 also shows equivalent processing parameters and properties of the resin, pipe and film of the poly-
ethylen resin produced in accordance with Comparative Example 1 in which the same chromium-based catalyst as
in Example 1 was employed in the production of a polyethylene resin, but with the catalyst having not been subjected
to a carbon monoxide reduction.

It will be seen that the density of the resin of Comparative Example 1 is the same as that of Example 1, but
that the melt index and the shear response have greater values that the corresponding values of Example 1. Most
importantly, the impact resistance of both the pipe and the film were significantly reduced as compared to the corre-
sponding properties of pipe and film made from the resin produced in accordance with Example 1. The pipe failed at
an internal pressurisation of 2.5 bars and the 10 micron film was penetrated by an 80 gram dart.

Comparative Example 2

Table 1 further shows equivalent processing parameters and properties of the resin and film of the polyethylene
resin produced in accordance with Comparative Example 2 in which the catalyst employed was a carbon monoxide-
reduced chromium-based catalyst having a low titanium content in the support. The catalyst employed was a catalyst,
identified as "catalyst 2" having a pore volume of 2.1cc/g and a specific surface area of 420 m2/g. The catalyst contained
0.9% Cr but only 1.45% Ti, each based on the weight of the catalyst. The catalyst, as for Example 1, was activated at
around 635°C and then subjected to a dry carbon monoxide reduction at a temperature of 370°C.

The resultant polyethylene was, as for Example 1, formed into 10 micron and 20 micron films and subjected
to the same impact tests as for Example 1. It will be seen from Table 1 that the films of Comparative Example 2 had
significantly lower film impact resistance than those of Example 1, the 10 and 20 micron films being penetrated by
darts of less than 30 g and 47 g respectively. The results of Example 1 and Comparative Example 2 show that the use,
in conjunction with carbon monoxide reduction, of a catalyst support having a titanium-containing support can give improved impact resistance performance to the resultant polyethylene resin.

COMPARATIVE EXAMPLE 3

In this Comparative Example, a different catalyst, catalyst 3, was employed having the properties specified
in Table 1. The catalyst was subjected to zero reduction and activation similar to those for Comparative Example 2 but
using the temperatures specified in Table 1. The resultant resin had the properties HLM, shear response and density
as specified in Table 1. A film produced from the resultant resin was tested for impact resistance as for the previous
Comparative Examples and the results are shown in Table 1. It may be seen that the use of a catalyst having a titanium
content of 5% by weight, i.e. greater than the 3% limit required by the present invention, yields reduced impact resist-
ance as compared to the present invention.

Claims

1. A process for producing polyethylene having impact resistance, the process comprising polymerising ethylene, or
copolymerising ethylene and an alpha-olefinic comonomer comprising from 3 to 10 carbon atoms, in the presence
of a chemically reduced chromium-based catalyst containing in a support thereof from 2 to 3wt% of titanium, based
on the weight of the catalyst, said polymerisation being carried out in the absence of a cocatalyst.

2. A process according to claim 1 wherein the support is a silica-titania support.

3. A process according to claim 1 or claim 2 wherein the carbon monoxide reduction has been performed at a tem-
4. A process according to claim 3 wherein the carbon monoxide reduction has been performed at a temperature of around 370°C.

5. A process according to any foregoing claim wherein the support contains around 2.3wt% titanium, based on the weight of the catalyst.

6. A process according to any foregoing claim wherein the catalyst has a pore volume of around 2.1cc/g and a specific surface area of around 510 m²/g.

7. A process according to any foregoing claim wherein the polyethylene has a high load melt index (HLMI) of from 5 to 12g/10min and a density of from 0.940 to 0.950g/cc.

8. A process according to any foregoing claim wherein the polyethylene has a shear response (SR) less than 80.

9. A chromium-based catalyst for the production of polyethylene by polymerising ethylene or copolymerising ethylene and an alpha-olefinic comonomer comprising from 3 to 10 carbon atoms, the catalyst being chemically reduced and containing in a support from 2 to 3wt% of titanium, based on the weight of the catalyst.

10. A chromium-based catalyst according to claim 9 wherein the support is a silica-titania support.

11. A chromium-based catalyst according to claim 9 or claim 10 wherein the support contains around 2.3wt% titanium, based on the weight of the catalyst.

12. A chromium-based catalyst according to any one of claims 9 to 11 wherein the catalyst has a pore volume of around 2.1cc/g and a specific surface area of around 510 m²/g.

Patentansprüche


2. Verfahren nach Anspruch 1, wobei der Träger ein Silica-Titanoxidträger ist.

3. Verfahren nach Anspruch 1 oder Anspruch 2, wobei die Kohlenmonoxidreduzierung bei einer Temperatur von 250 bis 500°C durchgeführt worden ist.


5. Verfahren nach einem vorhergehenden Anspruch, wobei der Träger etwa 2,3 Gew.% Titan, basierend auf dem Gewicht des Katalysators, enthält.

6. Verfahren nach einem vorhergehenden Anspruch, wobei der Katalysator ein Porenvolumen von etwa 2,1 cc/g und einen spezifischen Oberflächenbereich von etwa 510 m²/g hat.

7. Verfahren nach einem vorhergehenden Anspruch, wobei das Polyethylen einen hohen Beladungsschmelzindex (HLMI) von 5 bis 12g/10 Min und eine Dichte von 0,940 bis 0,950 g/cc hat.

8. Verfahren nach einem vorhergehenden Anspruch, wobei das Polyethylen eine Scherreaktion (SR) geringer als 80 hat.

9. Auf Chrom basierender Katalysator für die Herstellung von Polyethylen durch Polymerisieren von Ethylen oder

10. Auf Chrom basierender Katalysator nach Anspruch 9, wobei der Träger ein Silica-Titanoxidträger ist.

11. Auf Chrom basierender Katalysator nach Anspruch 9 oder Anspruch 10, wobei der Träger etwa 2,3 Gew.% Titan, basierend auf dem Gewicht des Katalysators, enthält.

12. Auf Chrom basierender Katalysator nach einem von Ansprüchen 9 bis 11, wobei der Katalysator ein Porenräumer von etwa 2,1 cc/g und einen spezifischen Oberflächenbereich von etwa 510 m²/g hat.

Revendications

1. Procédé pour préparer du polyéthylène possédant une résistance élevée aux chocs, le procédé comprenant le fait de polymériser de l'éthylène ou le fait de copolymériser de l'éthylène et un comonomère alpha-oléfinique comprenant de 3 à 10 atomes de carbone, en présence d'un catalyseur à base de chrome soumis à une réduction par voie chimique contenant, dans un support de ce dernier, du titane à concurrence de 2 à 3 % en poids, basés sur le poids du catalyseur, ladite polymérisation étant mise en œuvre en l'absence d'un cocatalyseur.

2. Procédé selon la revendication 1, dans lequel le support est un support à base de silice-dioxyde de titane.

3. Procédé selon la revendication 1 ou 2, dans lequel la réduction au monoxyde de carbone est mise en œuvre à une température de 250 à 500 °C.

4. Procédé selon la revendication 3, dans lequel la réduction au monoxyde de carbone est mise en œuvre de température d'environ 370 °C.

5. Procédé selon l'une quelconque des revendications précédentes, dans lequel le support contient du titane à concurrence d'environ 2,3 % en poids, basés sur le poids du catalyseur.

6. Procédé selon l'une quelconque des revendications précédentes, dans lequel le catalyseur possède un volume de pores d'environ 2,1 Cc/g et une aire de surface spécifique d'environ 510 m²/g.

7. Procédé selon l'une quelconque des revendications précédentes, dans lequel le polyéthylène possède un indice de fluidité à chaud sous charge élevée (HLMI) de 5 à 12 g/10 minutes et une densité de 0,940 à 0,950 g/Cc.

8. Procédé selon l'une quelconque des revendications précédentes, dans lequel le polyéthylène possède une réponse au cisaillement (SR) inférieure à 80.

9. Catalyseur à base de chrome pour la préparation de polyéthylène par polymérisation d'éthylène ou par copolymérisation d'éthylène et d'un comonomère alpha-oléfinique comprenant de 3 à 10 atomes de carbone, le catalyseur ayant été soumis à une réduction par voie chimique et contenant, dans un support de ce dernier, du titane à concurrence de 2 à 3 % en poids, basés sur le poids du catalyseur.

10. Catalyseur à base de chrome selon la revendication 9, dans lequel le support est un support à base de silice-dioxyde de titane.

11. Catalyseur à base de chrome selon la revendication 9 ou 10, dans lequel le support contient du titane à concurrence d'environ 2,3 % en poids, basés sur le poids du catalyseur.

12. Catalyseur à base de chrome selon la revendication 9 ou 11, dans lequel le catalyseur possède un volume de pores d'environ 2,1 Cc/g et une aire de surface spécifique d'environ 510 m²/g.