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(54) Title: LINEAR LOW DENSITY POLYETHYLENE, PROCESS FOR THE PREPARATION THEREOF AND FILMS MADE THEREFROM

(57) Abstract: A unimodal LLDPE formed from ethylene and at least one C_{3-12} alpha-olefin comonomer by single site catalysis having the following properties: a density of 915-950 kg /m^3;MFR_2 in the range 0.5 to 6; Mw/Mn in the range 2.5 to 4; a shear thinning SHI (1/100) of at least 1.7; a comonomer content of 2 to 10 wt% ; a melting temperature (Tm) of 115 to 128°C; and no long chain branching.

LINEAR LOW DENSITY POLYETHYLENE, PROCESS FOR THE PREPARATION THEREOF AND FILMS MADE THEREFROM

This invention relates to a unimodal linear low density polyethylene (LLDPE) having an ideal balance of sealing properties, impact, optical properties and processability without any long chain branching.

Unimodal LLDPE resins are widely used in packaging applications. LLDPE resins made using single site catalysis (mLLDPE's), e.g. metallocene catalysis, are of particular interest in the packaging of food and medical products in view of their low migration properties. Conventional Ziegler-Natta produced LLPDE's tend to have broad molecular weight distributions and suffer from migration of polymer into the product being packaged. Thus, whilst Ziegler-Natta LLDPE's may be used in food packaging they are less favoured in view of the potential migration problems.

It has been found that LLDPE resins made using single site catalysis (called mLLDPE's herein) do not suffer from this problem and are hence suitable for use in food packaging. Moreover, such mLLDPE's are known to possess excellent optical properties, i.e. they exhibit low levels of haze, and possess good impact properties, e.g. high dart drop values, on account of their narrow molecular weight distribution. However, these properties are achieved only at the expense of processability. In particular, mLLDPE's exhibit high pressure build up in the film blowing process.

An important property of the polymer is therefore its rheology. Rheology is a measure of non-Newtonian solid flow and it is crucial in any moulding or blowing operation that the polymer melt has a flow within certain limits to ensure that the final product properties are desirable. For example, the flow of the polymer melt must be sufficiently high to enable it to flow to all areas of a mould and thus to form an article of the desired shape. Also, the higher the flow of the

polymer melt the greater the speed at which it can be injected into the mould and the shorter the processing time. In film blowing, higher viscosity at low shear rate combined with a lower viscosity at higher shear rate is indicative of improved bubble stability and may allow increases in pressure in the blowing line and hence faster film line speeds.

One solution to the problem of high pressure build-up during film blowing is to introduce long chain branching into unimodal mLLDPE's and this has the added benefit of improving optical properties still further. However, the introduction of long chain branching leads to poorer mechanical properties, e.g. lower impact and stiffness properties.

The skilled polymer chemist is still searching therefore for a unimodal mLLDPE which has an ideal balance of sealing properties, impact, optical properties and processability but does not require the presence of long chain branching.

The present inventors have surprisingly found that a unimodal mLLDPE can be produced in a slurry loop reactor which has an ideal balance of sealing properties, impact, optical properties and processability without any long chain branching.

Thus, viewed from one aspect the invention provides a unimodal LLDPE formed from ethylene and at least one C_{3-12} alpha-olefin comonomer by single site catalysis having the following properties:

a density of 915-950 kg/m^3;
MFR_2 in the range 0.5 to 6;
Mw/Mn in the range 2.5 to 4;
a shear thinning SHI (1/100) of at least 1.7;
a comonomer content of 2 to 10 wt%;
a melting temperature (Tm) of 115 to 128°C;

and no long chain branching.

By no long chain branching is meant that no long chain branching is detectable using C^{13}NMR. Thus, the unimodal mLLDPE of this invention is completely free of long chain branching.

Viewed from another aspect the invention provides a process for the preparation of a LLDPE as hereinbefore described comprising polymerising ethylene and at least one C_{3-12} alpha-olefin comonomer in the presence of a single site catalysis.

The mLLDPE of the invention is unimodal. By unimodal is meant that its molecular weight profile (measured by GPC) comprises a single peak. The mLLDPE is therefore formed from one component. A single component is made by a single catalyst in a single polymerisation reaction stage.

The mLLDPE is by definition formed using a single site catalyst such as a metallocene catalyst. A wide variety of metallocene catalysts are known in the art and referred to in the literature. Suitable metallocenes and ways of preparing them are within the knowledge and skills of a person skilled in the field. Reference is made to EP-A-260 130, WO-A-9728170, WO-A-9846616, WO-A-9849208, WO-A-9912981, WO-A-9919335, EP-A-836608, WO-A-9856831, WO-A-00/34341, EP-A-423 101 and EP-A-537 130.

Preferably the mLLDPE is made using a hafnium metallocene such as a bis (n-butylcyclopentadienyl) hafnium dichloride or a bis (n-butylcyclopentadienyl) hafnium dibenzyl. Other potential catalysts are described in WO97/28170 and WO00/40620.

The mLLDPE may have a density of 915 to 950 kg/m^3, e.g. 920 to 950 kg/m^3, such as 920-945 kg/m^3, preferably in the range of from 920 to 930 kg/m^3, e.g. 922 to 927 kg/m^3 (ISO 1183).

The mLLDPE is formed from ethylene along with at least one C_{3-12} alpha-olefin comonomer, e.g. butene, hexene or octene. Preferably, the mLLDPE is an ethylene

hexene copolymer or ethylene butene copolymer. The amount of comonomer incorporated is preferably 2 to 10% wt relative to ethylene, especially 3 to 6% wt.

The MFR_2 (melt flow rate ISO 1133 at 190°C under a load of 2.16 kg) of the mLLDPE should preferably be in the range 0.5 to 4, preferably 1.0 to 2.0, e.g. 1.3 to 1.5 g/10min.

The mLLDPE should preferably have a weight average molecular weight (Mw) of 100,000-250,000, e.g. 110,000-160,000 (GPC). The Mw/Mn value should preferably be 2.5 to 4, e.g. 3.0 to 3.5 (GPC).

A further important properties of the mLLDPE's of the invention is their shear thinning index. Shear thinning index (SHI), which is correlating with molecular weight distribution but is independent of Mw, is calculated according to Heino ("Rheological characterization of polyethylene fractions" Heino, E.L., Lehtinen, A., Tanner J., Seppälä, J., Neste Oy, Porvoo, Finland, Theor. Appl. Rheol., Proc. Int. Congr. Rheol, 11th (1992), 1, 360-362, and ``The influence of molecular structure on some rheological properties of polyethylene'', Heino, E.L., Borealis Polymers Oy, Porvoo, Finland, Annual Transactions of the Nordic Rheology Society, 1995.)

The SHI value is obtained by calculating the complex viscosities η (1) and η (100) at a constant shear stress of 1 kPa and 100 kPa, respectively. The shear thinning index SHI(1/100) is defined as the ratio of the two viscosities η (1) and η (100).

The SHI ratio is thus:

$$\eta^* (G^* = 1\text{kPa}) / \eta^* (G^* = 100\ \text{kPa})$$

wherein η^* is complex viscosity and is given by the ratio G^*/w where w is frequency and G^* is the absolute value of the complex modulus and is given by the ratio

$(G'^2 + G''^2)^{½}$ wherein G' is the storage modulus and G'' is the loss modulus. G' and G'' are measured according to ISO 6721-1 at 190°C under 1 (G') or 100 kPa (G'') and under a nitrogen atmosphere (e.g. using a RDA II Dynamic Rheometer). The person skilled in the art is aware of how to measure this property.

The mLLDPE should have a shear thinning SHI (1/100) of at least 1.7, e.g. 1.7 to 2.5, especially, 1.7 to 2.0.

The melting temperature of the polymer should be in the range 115 to 128°C, e.g. 115 to 125°C, preferably 116 to 124°C, e.g. 117 to 123°C.

The polymers of the invention can be manufactured in a slurry loop reactor using a single site catalyst, e.g. metallocene catalyst, as described above. For slurry reactors, the reaction temperature will generally be in the range 60 to 110°C (e.g. 85-110°C), the reactor pressure will generally be in the range 5 to 80 bar (e.g. 50-65 bar), and the residence time will generally be in the range 0.3 to 5 hours (e.g. 0.5 to 2 hours). The diluent used will generally be an aliphatic hydrocarbon having a boiling point in the range -70 to +100°C. In such reactors, polymerisation may if desired be effected under supercritical conditions.

Preferably, the polymer is produced in a continuously operating loop reactor where ethylene is polymerised in the presence of a polymerisation catalyst as stated above and a chain transfer agent such as hydrogen. The diluent is typically an inert aliphatic hydrocarbon, preferably isobutane or propane.

The polymer may contain various standard polymer additives such as antioxidants, UV stabilisers and polymer processing agents such as fluoroelastomers.

The polymer of the invention may be injection moulded or blow moulded as is known in the art. However, the polymer is advantageously used in the manufacture of film. Thus, the polymer can be blown

into films using conventional film blowing techniques. The polymer of the invention can be used on its own although preferably films made using the polymer of the invention will also comprise a low density polyethylene component (LDPE). LDPE is an ethylene polymer produced in a high pressure radical process known in the art and is different from an LLDPE. The inclusion of an LDPE component improves the haze of the film. The amount of LDPE present (relative to the unimodal mLLDPE) may range from 3 to 20% wt, e.g. 5 to 15% by weight especially about 10% by weight. Conveniently therefore the ratio mLLDPE to LDPE in the outer layer is about 9:1.

The LDPE may have a density of 915-935 kg/m^3, especially 922-930 kg/m^3. The MFR_2 of the LDPE may range from 0.3 to 2.5 g/10 min, e.g. 0.5 to 2.0 g/10 min. Suitable LDPE's are available commercially from Borealis as FT or FA Grades. Of particular utility is FT5270, FA5240 and FA5223.

For film formation using a polymer mixture it is important that any different polymer components be intimately mixed prior to extrusion and blowing of the film as otherwise there is a risk of inhomogeneities, e.g. gels, appearing in the film. Thus, it is especially preferred to thoroughly blend the components, for example using a twin screw extruder, preferably a counter-rotating extruder prior to extrusion and film blowing.

The film of the invention will typically be produced by extrusion through an annular die, blowing into a tubular film by forming a bubble which is collapsed between nip rollers after solidification. This film can then be slit, cut or converted (e.g. gusseted) as desired. Conventional film production techniques may be used in this regard. Typically the outer and core layer mixtures will be coextruded at a temperature in the range 160°C to 240°C, and cooled by blowing gas (generally air) at a temperature of 10 to

50°C to provide a frost line height of 2 to 8 times the diameter of the die. The blow up ratio should generally be in the range 2 to 4, preferably 2.5 to 3.

The polymer of the invention, along with any LDPE may form a complete film or a layer (or layers) of a multilayer film. It may for example be convenient to combine a film layer comprising the polymer of the invention with a barrier layer, e.g. a layer comprising polyamide. Such a barrier layer would make the film impervious to, for example, water and oxygen whilst the film layer comprising the polymer of the invention provides an ideal outer layer with good sealing, optical, and mechanical properties. Such a film is ideal for food packaging where barrier properties are desirable.

Films made using the polymer of the invention exhibit high dart impact strengths and tear strengths, especially in the transverse direction. Thus, for a 40 micron film comprising 100% polymer of the invention, Dart drop F50 (ISO 7765/1) may be at least 180 g, e.g. at least 300 g. Elmendorf Tear resistances in the machine direction for such a film may be at least 2.0 N (ISO 6383/2). In the transverse direction they may be at least 4 N.

The polymer also exhibits ideal stiffness measured as sec modulus in the transverse (TD) or machine (MD) direction. The sec modulus (TD) may be greater than 150 MPa, e.g. in the range 200 to 300 MPa, especially 220 to 280 MPA. In the machine direction the sec modulus may greater than 150 MPa, e.g. in the range 250 to 300 MPa.

High stiffness is conventionally only achievable at the expense of sealing properties, i.e. the sealing window of stiff polymers tends to be narrow. Surprisingly, however, the polymers of the present invention still have a broad sealing window. As shown in Figure 1, the hot tack properties of the polymers of the invention are excellent.

The tensile strain at break properties of the films of the invention are also good, e.g. greater than 600%. Tensile strength values in either the machine or transverse direction may be greater than 40 MPa.

The films exhibit excellent haze properties, e.g. less than 40%, preferably less than 35%, especially less than 30% (ASTM D1003) for a 40 micron film despite having broad composition distribution. Figure 2 shows the composition distribution of polymers of the invention. Films made from the polymer of the invention exhibit broad composition distribution and hence would be expected to exhibit poor haze values associated with such a composition. Surprisingly, the films made from the polymers claimed have low haze values.

Thus viewed from a further aspect the invention provides a film made from the mLLDPE as hereinbefore defined having

a Dart drop F50 (ISO 7765/1) of at least 180 g;
an Elmendorf Tear resistance in the machine direction of at least 2.0 N;
a sec modulus (TD) greater than 150 MPa, e.g. in the range 200 to 300 MPa;
a sec modulus (MD) greater than 150 MPa, e.g. in the range 250 to 300 MPa;
a haze of less than 40%.

The films of the invention have a wide variety of applications but are of particular utility in packaging of food, medical devices and in heavy duty packaging. The films may act as shrink films and are thus suitable for shrink applications, e.g. to package goods for transportation.

The invention will now be described further with reference to the following non-limiting examples and Figures. Figure 1 shows the hot tack properties of the polymers of Examples 1 and 2.

Figure 2 shows the composition distribution shown by TREF of two polymers of the invention.

Analytical Tests

Density is measured according to ISO 1183

MFR2/21 are measured according to ISO 1133 at 190°C at loads of 2.16 and 21.6 kg respectively.

Mw, Mn, and Mw/Mn are measured by GPC.

Haze is measured according to ASTM D 1003

Gloss is measured according to ASTM D 2457

Tensile Strain at break and tensile strength are measured according to ISO 527-3

Sec modulus is measured according to ASTM D 882-A

Impact resistance is determined on Dart-drop (g/50%). Dart-drop is measured using ISO 7765-1, method "A". A dart with a 38 mm diameter hemispherical head is dropped from a height of 0.66 m onto a film clamped over a hole. If the specimen fails, the weight of the dart is reduced and if it does not fail the weight is increased. At least 20 specimens are tested. The weight resulting in failure of 50% of the specimens is calculated.

Tear resistance (determined as Elmendorf tear (N))
The tear strength is measured using the ISO 6383 method. The force required to propagate tearing across a film specimen is measured using a pendulum device. The pendulum swings under gravity through an arc, tearing the specimen from pre-cut slit. The specimen is fixed on one side by the pendulum and on the other side by a

stationary clamp. The tear strength is the force required to tear the specimen.

Hot tack is a method for measuring the strength of heat seal of film and lamination immediately after sealing operation. This property is measured on a DTC International Hot tack tester model 52-D, w-4236 according to an internal method. Samples are cut with a width of 15mm. The sealing time is 0.5sec, a delay time is 0,1sec and a sealing pressure of 90N. The sealing at different temperature are measured and for each test temperature 5 parallels are taken. The specimens have been conditioned in min- 24 hours before testing.

Thermal properties were measured according to ISO11357-1 on a Perkin Elmer DSC-7. Heat from -10°C to 200°C at 10°C/min. Hold for 10 min. at 200°C. Cool from 200°C to -10°C at 10°C per min.

The comonomer content has been measured on a melt pressed 0,2mm thick films on a Perkin Elmer Spectrum GX using the absorption at 1377 cm-1 (total methyl content). The method was calibrated with samples analysed by C13 NMR measurements.

Example 1

Ethylene hexene resins were produced using bis(n-butylcyclopentadienyl) hafnium dibenzyl catalyst in a slurry loop reactor at the following conditions:

Pressure 42 bar
C2 amount 4 wt%
C6/C2: 0.35
Temp. 86°C
Residence time: 40 to 60 mins

The resulting polymer grade A has a MFR_2 of 1.3 g/10min and a density of 922 kg/m^3.

Example 2

The process of example 1 was repeated except the polymerisation temperature was increased to 90°C and the C6/C2 ratio was 0.5. The resulting polymer Grade B has an MFR_2 of 1.3 g/10min and a density of 927 kg/m^3.

The properties of Grades A and B are given below:

Table 1

Grade		Grade A	Grade B
MFR2	g/10min	1.3	1.3
Density	kg/m3	922	927
DSC melting point	°C	117	120
Mw/Mn		3.2	3.2
SHI (1/100)		1.9	1.9
C6 WT%	Wt%	5.3	3.6

The SHI is an index describing the rheological broadness of the polymer and is measured as described in the description. A rheologically broader polymer has improved processability.

Hot Tack

Hot tack results for Grades A and B are presented in Figure 1.

TREF

Fractionation of the polyethylene samples was achieved by using analytical TREF. The sample was dissolved in xylene (2-4 mg/ml) at 135°C and injected into the column at 135°C, and the latter was then cooled to 15°C at a

rate of 1.5 K/h. The column was subsequently eluted with 1,2,4-trichlorobenzene (TCB) at a flow rate of 0.5 ml /min while the temperature was increased from 20°C to 130°C over 4,5 h. The output, detected with an IR detector operating at a wavelength of 3.41mm, was presented as a fractogram normalized to constant area. The results are presented in Figure 2.

Example 3 Films

40 micron films of Grades A and B were produced on a Ankutec film line (50 mm die diameter), die gap 1,5/2,6 mm, BUR 2.5, Temp.setting 210°C. Further films were produced at the same thickness using the same conditions where 5 wt% LDPE was added.

Their properties are given in Table 2 below.

Table 2

Grade		Grade A	Grade B
Dart drop (g)	g	380	210
Tear resistance MD/TD	N	2.5/5	2.4/5.5
Gloss, 60° (pure mLLD)		95	80
Haze (pure mLLD)	%	10	20
Haze (5% LDPE added)	%	5	6
Sec Mod (0.05-1.05) MD/TD	MPa	170/180	230/270
Tensile Strength MD/TD	MPa	46/46	51/48
Tensile Strain at Break (MD/TD)	%	630/640	640/660

Claims

1. A unimodal linear low density polyethylene (LLDPE) formed from ethylene and at least one C_{3-12} alpha-olefin comonomer by single site catalysis having the following properties:

a density of 915-950 kg/m^3;
MFR_2 in the range 0.5 to 6;
Mw/Mn in the range 2.5 to 4;
a shear thinning SHI (1/100) of at least 1.7;
a comonomer content of 2 to 10 wt%;
a melting temperature (Tm) of 115 to 128°C;

and no long chain branching.

2. A LLDPE as claimed in claim 1 having a density in the range 920 to 950 kg/m^3 and a melting temperature in the range 115 to 125°C.

3. A LLDPE as claimed in claim 2 having a density in the range 920 to 930 kg/m^3 and an MFR_2 in the range 0.5 to 2.0 g/10 min.

4. A LLDPE as claimed in claim 2 having a density in the range 922 to 930 kg/m^3 and an MFR_2 in the range 1.0 to 2.0 g/10 min.

5. A LLDPE as claimed in any one of claims 1 to 3 wherein said C_{3-12} comonomer is butene or hexene.

6. A LLDPE as claimed in any one of claims 1 to 5 wherein the comonomer content is 3 to 6 wt%.

7. A LLDPE as claimed in any one of claims 1 to 5 being made using bis(n-butylcyclopentadienyl) hafnium dibenzyl.

8. A film comprising an LLDPE a claimed in any one of claims 1 to 7.

9. A film as claimed in claim 8 having:

a Dart drop F50 (ISO 7765/1) of at least 180 g;
an Elmendorf Tear resistances in the machine direction of at least 2.0 N;
a sec modulus (TD) greater than 150 MPa;
a sec modulus (MD) greater than 150 MPa;
a haze of less than 40%.

10. A film as claimed in claim 9 having a
a sec modulus (TD) in the range 200 to 300 MPa; and
a sec modulus (MD) in the range 250 to 300 MPa.

11. A film as claimed in claim 8 to 10 further comprising LDPE.

12. A process for the preparation of a LLDPE as claimed in claim 1 to 7 comprising polymerising ethylene and at least one C_{3-12} alpha-olefin comonomer in the presence of a single site catalysis to give an LLDPE having the following properties:

a density of 915-950 kg/m^3;
MFR_2 in the range 0.5 to 6;
Mw/Mn in the range 2.5 to 4;
a shear thinning SHI (1/100) of at least 1.7;
a comonomer content of 2 to 10 wt%;
a melting temperature (Tm) of 115 to 128°C;

and no long chain branching.

13. A process as claimed in claim 12 which takes place in a slurry loop reactor.

14. A process as claimed in claim 12 or 13 wherein said single site catalyst is bis(n-butylcyclopentadienyl) hafnium dibenzyl.

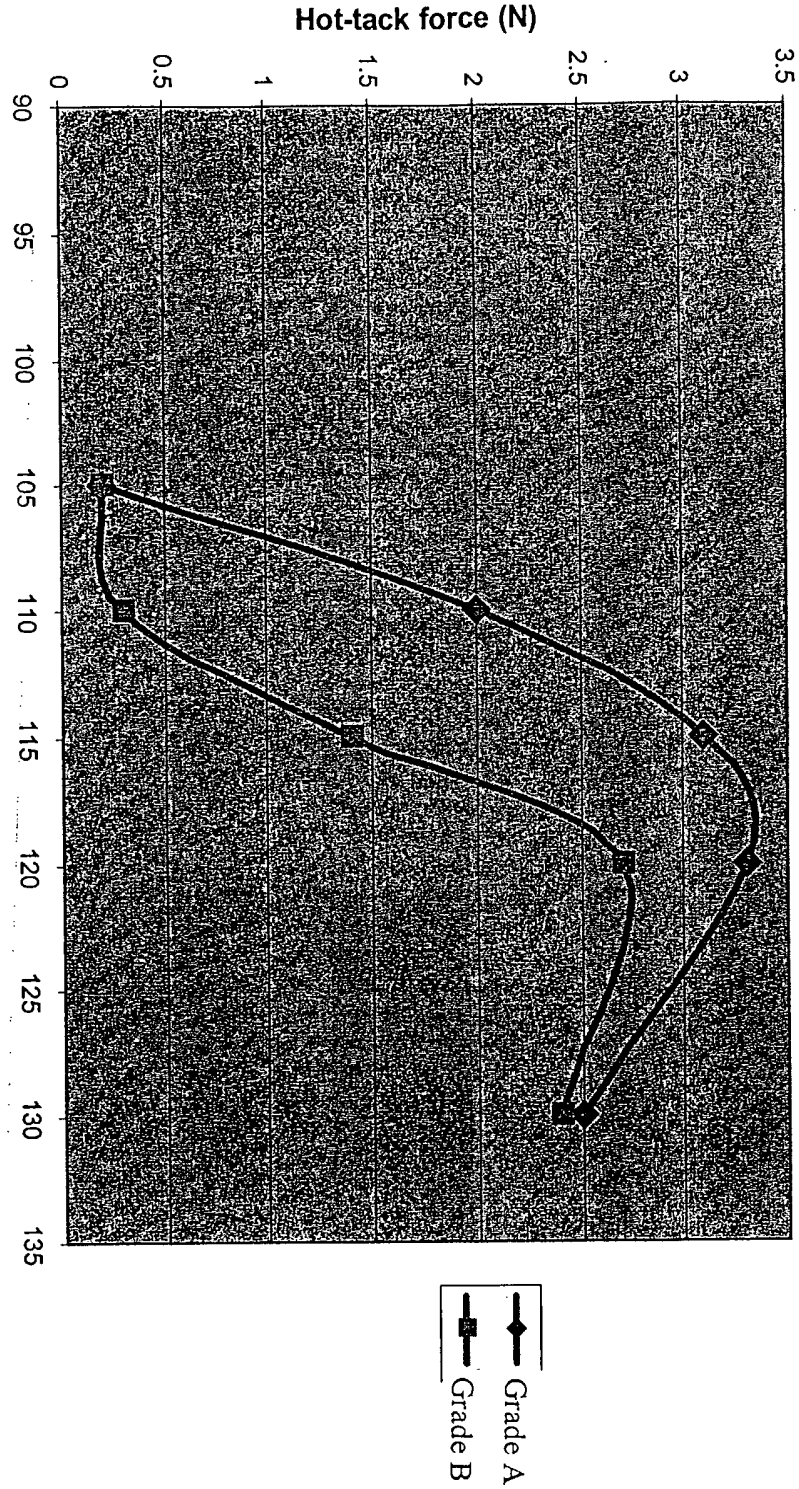
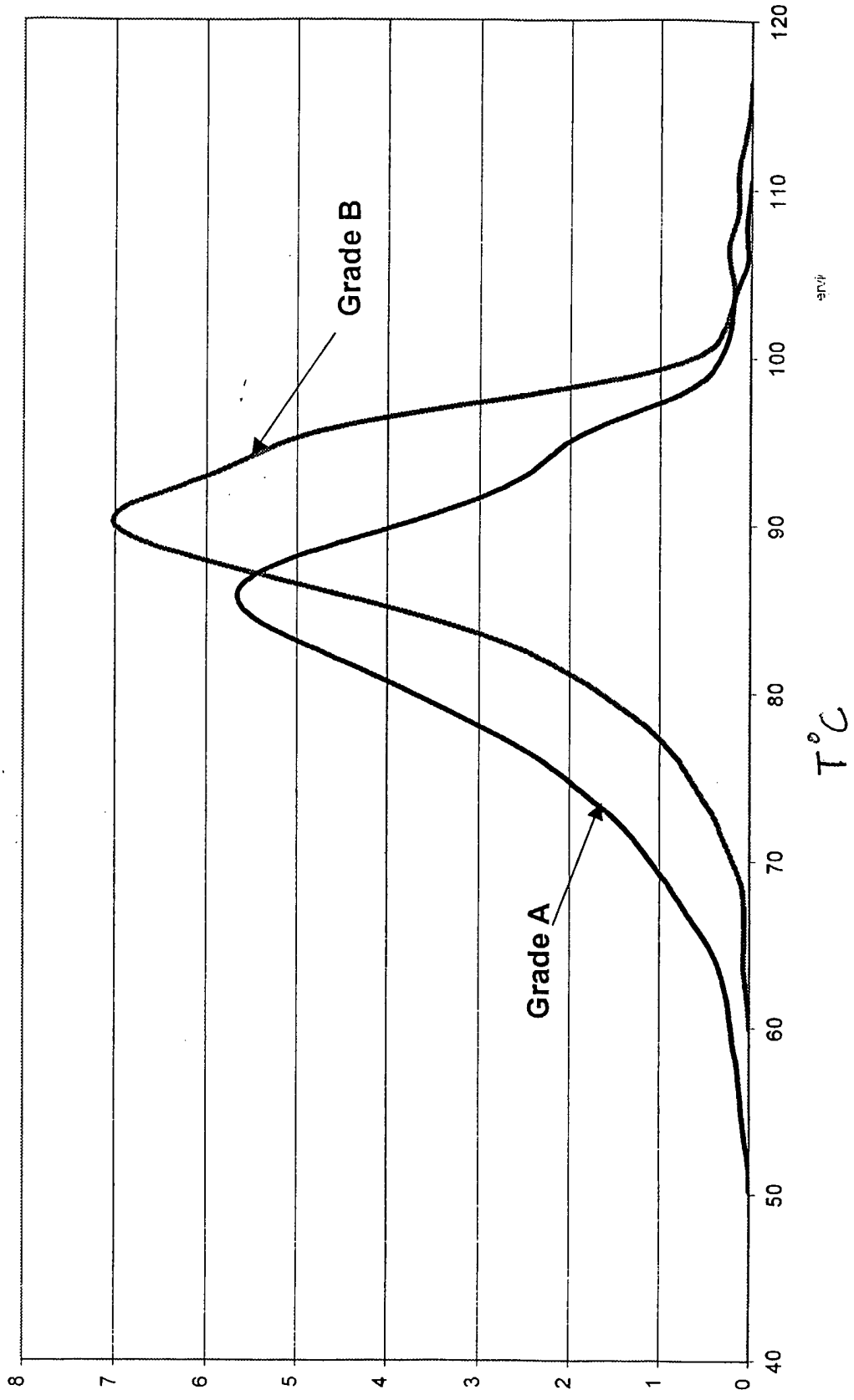

Hot-tack force (N)
0
0.5
1
1.5
2
2.5
3
3.5
Temperature (degree C)
90
95
100
105
110
115
120
125
130
135
Grade A
Grade B

Figure 1

Figure 2



INTERNATIONAL SEARCH REPORT

International Application No
[redacted]/EP2005/011223

A. CLASSIFICATION OF SUBJECT MATTER
C08F210/16 C08J5/18

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

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

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2002/040114 A1 (LOVEDAY DONALD R ET AL) 4 April 2002 (2002-04-04) paragraph '0072! - paragraph '0080!; claims; examples 3A,to,6B; tables	1-14
X	EP 1 097 949 A (JAPAN POLYCHEM CORPORATION) 9 May 2001 (2001-05-09) claims; examples; table 1	1-14
X	US 2004/077810 A1 (MARECHAL PHILIPPE) 22 April 2004 (2004-04-22) paragraph '0016!; claims; tables II,III	1-14
X	US 6 319 961 B1 (TAKAHASHI MAMORU) 20 November 2001 (2001-11-20) claims; table 1	1-7, 12-14

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

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
11 January 2006	17/01/2006

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3

Form PCT/ISA/210 (second sheet) (January 2004)

INTERNATIONAL SEARCH REPORT

International Application No
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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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