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(54) **Title:** MULTILAYER POLYPROPLYENE FILM

(57) **Abstract:** Multilayer film comprising at least a skin layer, a core layer and an inner layer, whereby the inner layer comprises a single site catalyst derived (SSC) random propylene ethylene copolymer having - a melting temperature (Tm) from 120°C to 144°C, - a content of units derived from ethylene in an amount of 1.5 to 6.0 wt.-%, - the melting temperature (Tm) fulfilling the following equation $Tm < 156\,°C - [5.2 \times C2\ \text{content in wt.-%}]\,°C$ wherein C2 content stands for the content of units derived from ethylene; and - a xylene cold soluble content (ISO 16152, 1st ED, 2005-07-01; 25°C) of preferably below 30 wt.-% wherein the multilayer film is free of phthalic acid esters as well as decomposition products thereof.

WO 2020/245251 A2

yer polyprop

Multila   ylene film

Field of the invention

5   The instant invention relates to polypropylene soft multilayer films having good
optical properties as well as low SIT and a method for producing the same and use
thereof.

Background

10

Polymers, especially polypropylene, are widely used film, particularly in medical
pouch systems due to their excellent performance, such as softness, transparency,
and biocompatibility with human beings and animals. The currently used
polypropylene based films and pouches suffer from limitations as regards
15   transparency especially after sterilization. There is further a tendency to avoid any
potentially health and environmentally harmful compounds such as phthalic acid
esters. Recently this has been addressed by phthalate free catalyst systems.
Typical film for medical pouch systems have three layers, namely skin layer, core
layer and inner layer. From a functional perspective the inner layer guarantees good
20   sealing properties.

Typically the inner layer is derived from Ziegler catalysts and is a C2C3 random
copolymer with relatively low melting temperature (Tm). However, due to the
technology itself, the properties windows are limited. When aiming at low sealing
25   initiation temperature (SIT), it is necessary to increase ethylene content, whereby
the XCS goes up and sterilization deteriorates.
There are some alternative materials with low sealing initiation temperature (SIT) on
the market, for example C2C3C4-terpolymers. However, due to some regulations,
the application of C2C3C4-terpolymers is extremely limited. There was a long felt
30   need to get rid of terpolymers.

US 7537829 B2 concerns a multi-layer film for packaging, comprising a core layer
containing a core polymer and a soft polymer, a tie layer comprising a tie layer
polymer such as a C2C8 alpha olefin and a sealant layer. The exemplified films
35   comprise soft Adflex grades and are non-transparent.
WO0142009 describes a multilayer film free of PVC comprising three layers.
DE202013103803U1 is concerned with a transparent multilayer film including also a

sealing layer. JP2007245490 concerns multilayer film allowing the provision of medical soft bags.

WO 2010117148 A2 and WO 2010117150 A2 concern three-layer film constructions with an outer layer of PP (homo- or copolymer) and a central layer of 10-60 wt% of

5   PP copolymer and 40-90 wt% thermoplastic elastomer (TPE; chosen from hydrogenated styrene-isoprene-butadiene (SIBS) copolymer, hydrogenated styrene-butadiene-styrene (SBS) copolymer, hydrogenated styrene-isoprene-styrene (SIS) copolymer, hydrogenated styrene-ethylene-butadiene-styrene (SEBS) copolymer, hydrogenated styrene-ethylene-propylene-styrene (SEPS) copolymer, hydrogenated

10   styrene-ethylene-ethylene-propylene-styrene (SEEPS) copolymer, hydrogenated styrene-butadiene (SBC) copolymer, hydrogenation styrene-ethylene-propylene-styrene (SBPS) copolymer and their combination), and an inner layer of PP (homo- or copolymer), 10-30 wt% LLDPE and 1-10 wt% TPE. The LLDPE comprised in the inner layer constitutes a major problem for high temperature applications.

15   EP 2546298 B1 concerns monolayer unoriented film comprising at least 70 wt.-% of an heterophasic propylene copolymer (RAHECO), said RAHECO comprising a matrix (M) being a random propylene copolymer (R-PP) and an elastomeric propylene copolymer (E) dispersed in said matrix (M), wherein the RAHECO has (a) an MFR2 (230 °C) measured according to ISO 1133 in the range of 2.0 to 15.0

20   g/10min, (b) a melting temperaturemelting temperature (Tm) determined by differential scanning calorimetry (DSC) in the range of 130 to 150 °C, (c) a xylene cold soluble content (XCS) determined according ISO 16152 (25 °C) in the range of 25 to 50 wt.-%, (d) a comonomer content in the range of 10.0 to 15.0 wt.-%, wherein further the xylene cold soluble content (XCS) of the heterophasic propylene

25   copolymer (RAHECO) has (e) a comonomer content in the range of 20 to 30 wt.-% and (f) an intrinsic viscosity (IV) determined according to DIN ISO 1628/1, (in Decalin at 135 °C) in the range of 0.8 to below 2.0 dl/g.

EP 2831168 B1 describes discloses three layer film having an outer layer, core layer and a sealing layer. The core layer has been described to be layer (L1), said layer

30   (L1) comprises at least 70 wt.-% of a polymer composition (Co), said composition (Co) comprises (a) a propylene copolymer (A) having (a1) a melt flow rate MFR2 (230 °C) measured according to ISO 1133 in the range of more than 2.0 to 15.0 g/10min, (a2) a comonomer content in the range of more than 7.5 to 16.5 wt.-%, and (a3) a xylene cold soluble content (XCS) determined according ISO 16152 (25 °C)

in the range of 25.0 to 55.0 wt.-%, wherein (a4) the comonomer content of xylene cold soluble (XCS) fraction of the propylene copolymer is in the range of 14.0 to 30.0 wt.-%,and (b) a styrenic based elastomer(s) (B) having a styrene content in the range of 5 to equal or below 15 wt.-%, wherein the polypropylene (A) has a melting temperature in the range of 145 to 160°C. The haze values reported still show room for optimization.
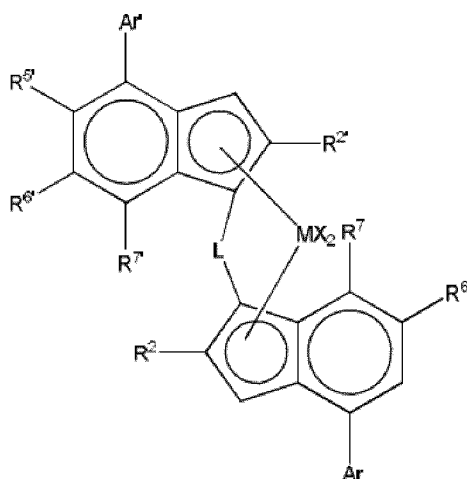
WO2017/19866 concerns heterophasic propylene copolymers (RAHECO) being made with a phthalate free catalyst for use in polypropylene film, particularly medical packaging film having good softness but unfortunately somewhat deteriorated haze when compared with similar heterophasic propylene copolymers being made by traditional phthalate containing catalysts.

Moreover traditional material show a conflict of aims when styrene based thermoplastic elastomers (TPEs) are added to heterophasic propylene copolymers (RAHECOs) as the balance of softness and haze is limited.

Thus there was still the need for a multilayer film with relatively low SIT, good optics, low extractables, and excellent sterilization properties. Particularly there was the need for a multilayer film with relatively low SIT and good optics before and specifically after sterilization.

Summary of the invention

The present invention is based on the surprising finding that these object at least in part can be achieved by using polymers for the skin and core layer obtained from Ziegler Natta catalyst having internal citraconate donors together with polymers for the inner layer preferentially having an unique Tm – C2 ratio such as obtained preferably from single site catalysts comprising

(i) a complex of formula (I):

wherein

M is zirconium or hafnium;

each X is a sigma ligand;

L is a divalent bridge selected from -R'2C-, -R'2C-CR'2-, -R'2Si-, -R'2Si-SiR'2-, -R'2Ge-,

wherein each R' is independently a hydrogen atom, C1-C20-hydrocarbyl, tri(C1-C20- alkyl)silyl, C6-C20-aryl, C7-C20-arylalkyl or C7-C20-alkylaryl;

R2 and R2' are each independently a C1-C20 hydrocarbyl radical optionally containing one or more heteroatoms from groups 14-16;

R5' is a C1-20 hydrocarbyl group containing one or more heteroatoms from groups 14-16,optionally substituted by one or more halo atoms;

 R6 and R6' are each independently hydrogen or a C1-20 hydrocarbyl group optionally containing one or more heteroatoms from groups 14-16; wherein R6´ is preferably a tertiary alkyl group,

R7 is hydrogen or C1-20 hydrocarbyl group optionally containing one or more heteroatoms from groups 14-16;

 R7´ is hydrogen;

Ar is independently an aryl or heteroaryl group having up to 20 carbon atoms optionally substituted by one or more groups R1;

Ar' is independently an aryl or heteroaryl group having up to 20 carbon atoms optionally substituted by one or more groups R1;

each R1 is a C1-20 hydrocarbyl group or two R1 groups on adjacent carbon atoms taken together can form a fused 5 or 6 membered non aromatic ring with the Ar group, said ring

being itself optionally substituted with one or more groups R4;

5   each R4 is a C1-20 hydrocarbyl group;

and

(ii) a cocatalyst comprising at least one or two compounds of a group 13 metal, e.g.

10   Al and/or boron compound.

The present invention therefore provides

a multilayer film comprising at least a skin layer, a core layer and an inner layer,

15

the skin layer comprising a homo polypropylene or a random propylene ethylene copolymer including up to 2.5 wt.-% units derived from ethylene, the homopolypropylene or the random propylene ethylene copolymer having a MFR_2 (ISO1133, 230°C) of 2.0 to 20g/10min and a melting temperature (Tm) of 145 to 170

20   °C;

the core layer comprising a mixture obtainable by melt blending
20 to 80 wt.-% of a random heterophasic copolymer and 20 to 80 wt.-% of styrene based thermoplastic elastomer (TPE),

25   whereby the random heterophasic copolymer comprises a matrix phase and dispersed therein an elastomer phase, whereby the matrix phase is formed by a random propylene ethylene copolymer and whereby the random heterophasic copolymer has
a melting temperature (Tm) of 130 °C – 145 °C, and

30   a flexural modulus of 250 to 850 MPa when measured on injection molded specimens (23°C, 50% humidity, ISO 178)
and includes an ethylene propylene copolymer rubber; and
whereby the styrene based thermoplastic elastomer (TPE) has a styrene content of from 5 to 20 wt.-%, and

the inner layer comprising a single site catalyst derived (SSC) random propylene ethylene copolymer having a melting temperature (Tm) from 120 °C to 144°C, a content of units derived from ethylene in an amount of 1.5 to 6.0 wt.-%,

5   the melting temperature (Tm) fulfilling the following equation

$$Tm < 156\ °C - [5.2 \times C2\ \text{content in wt.-}\%]\ °C$$

wherein C2 content stands for the content of units derived from ethylene;

10   and

a xylene cold soluble content (ISO 16152, 1st ED, 2005-07-01; 25°C) of preferably below 30 wt.-%

wherein the multilayer film is free of phthalic acid esters as well as decomposition products thereof.

15

"Free of phthalic acid esters as well as decomposition products thereof" indicates absence of such components within the well accepted understanding in the art. "Free of phthalic acid esters as well as decomposition products thereof" indicates a maximum of 10 µg/kg, i.e. 10 ppb by weight. Such values have been reported for

20   common soil and river sediments. It is well known for many years that the actual detection limit is lower than the environmental background concentration. Attention is drawn to H. Fromme, T. Küchler, T. Otto, K. Pilz, J. Müller, A. Wenzel Water Research 36 (2002) 1429 – 1438 which is incorporated by reference herewith. Detection is straightforward by gas chromatography coupled with one- or two

25   dimensional mass spectrometry (GC-MS respectively GC-MS/MS) optionally preceded by enrichment on a suitable adsorption material.

Propylene ethylene copolymers denote copolymers containing at least 50 mol-% of units derived from propylene. Ethylene propylene copolymers denote copolymers

30   containing at least 50 mol-% of units derived from ethylene. A random heterophasic copolymer denotes a copolymer comprising two distinctive phases, namely a matrix phase and dispersed therein an elastomer phase, whereby the matrix phase is formed by a random propylene ethylene copolymer. Heterophasic nature can be identified by the presence of at least two distinct glass transition temperatures. The

abbreviation TPE stands for thermoplastic elastomer. A styrene based thermoplastic elastomer (TPE) denotes a styrenic block copolymer having a basic structure A-B-A, whereby A stands for polystyrene and B stands for an elastomeric phase. A typical example is SEBS, i.e. styrene ethylene butylene styrene block copolymer.

5

In a particularly preferred aspect, the multilayer film according to present invention is further characterized in that the random heterophasic copolymer forming, together with styrene based thermoplastic elastomer (TPE), the core layer has a xylene cold soluble fraction (XCS) having an intrinsic viscosity of 1.0 to 2.0 dl/g (DIN ISO

10   1628/1, 10/1999; Decalin, 135°C). This IV(XCS) concerns the random heterophasic copolymer before melt-blending with the styrene based thermoplastic elastomer (TPE).

The multilayer film according to the present invention preferably has a total

15   thickness of 50 to 500 micrometer, preferably 50 to 400 micrometer, more preferably 50 to 300 micrometer, even more preferably 50 to 250 micrometer and most preferably 100 to 200 micrometer.

In a further aspect, the multilayer film is characterized by a specific film layer

20   thickness distribution. The core layer preferably has a thickness of 50 to 90 % with respect to the thickness of the multilayer film. The percentage given insofar pertains to the individual layer thickness versus the total multilayer film thickness. The core layer more preferably has a thickness of 50 to 85 % with respect to the thickness of the multilayer film, more preferably 70 to 85% and most preferably 75 to 80 % with

25   respect to the thickness of the multilayer film. It should be understood any of these percentages given may be combined with any of the preferred total thickness values as given above. The combination of preferred thicknesses and preferred percentages of the same level is however particularly preferred.

30   In yet a further aspect, the thicknesses of the skin layer is preferably 5 to 25%, more preferably 10 to 25% and most preferably 10 to 15% with respect to the thickness of the multilayer film.

Independent therefrom the thicknesses of the inner layer is preferably 5 to 25%, more preferably 10 to 25% and most preferably 10 to 15% with respect to the thickness of the multilayer film.

5   Most preferably, the skin layer and the inner layer have the same percentage with respect to the thickness of the multilayer film, i.e. both have 5 to 25%, more preferably 10 to 25% and most preferably 10 to 15% with respect to the thickness of the multilayer film.

10   It is possible that one or more of the layers, i.e. skin layer, core layer and/or inner layer splits into two or even more sub-layers. In such case, the thickness shall indicate the total thickness of the respective sub-layers. In a further aspect, the multilayer film according to the present invention preferably consists of three layers, namely skin layer, core layer and inner layer. Any of these three layers may split into

15   two or more sub-layers.

The skin layer preferably consists of the homo polypropylene or random propylene ethylene copolymer as defined herein. This means presence of further polymeric components in substantial amounts is preferably excluded. However, the presence

20   of stabilizers in an amount of up to 3 wt.-% with respect the total weight of the skin layer and/or the presence of further polymeric components in an amount of up to 3 wt.-% with respect the total weight of the skin layer shall be possible. In other words, "skin layer preferably consists of the homo polypropylene or random propylene ethylene copolymer as defined herein" as a matter of definition also allows the

25   presence of up to 3 wt.-% stabilizers and/or up to 3 wt.-% polymeric components. As a typical example for a further polymeric compontent used in minor amounts of for example 1 wt.-% masterbatch polymer(s) may be mentioned.

The core layer preferably comprises, more preferably consists of the mixture

30   obtainable by melt blending 20 to 80 wt.-% of a random heterophasic copolymer and 20 to 80 wt.-% of styrene based thermoplastic elastomer (TPE). The core layer preferably consists of the mixture obtainable by melt blending 20 to 80 wt.-% of a random heterophasic copolymer, more preferably by melt blending 20 to 80 wt.-% of

a random heterophasic copolymer and 20 to 80 wt.-% of styrene based thermoplastic elastomer (TPE).

Again the presence of further polymeric components in substantial amounts is preferably excluded. Particularly, the presence of stabilizers in an amount of up to 3 wt.-% with respect the total weight of the core layer shall be possible and/or the presence of further polymeric components in an amount of up to 3 wt.-% with respect the total weight of the skin layer shall be possible and within the meaning of "consists of" as a matter of definition.

The core layer layer more preferably comprises, yet more preferably consists of the mixture obtainable by melt blending 40 to 20 wt.-% of a random heterophasic copolymer and 60 to 80 wt.-% of styrene based thermoplastic elastomer (TPE). It is a particularly surprising finding of the present invention that addition of a styrene based thermoplastic elastomer (TPE) does not deteriorate haze but improves both, softness and haze.

The inner layer preferably consists of the single site catalyst derived (SSC) random propylene ethylene copolymer as specified above, i.e
having

-        a melting temperature (Tm) from 120 °C to 144°C,

-        a content of units derived from ethylene in an amount of 1.5 to 6.0 wt.-%,

-        the melting temperature (Tm) fulfilling the following equation

$$Tm < 156\ °C - [5.2 \times C2\ \text{content in wt.-\%}]\ °C$$

wherein C2 content stands for the content of units derived from ethylene;
and

-        a xylene cold soluble content (ISO 16152, 1st ED, 2005-07-01; 25°C) of
            preferably below 30 wt.-%

, Again "consists of" shall exclude the presence of further polymeric components in substantial amounts but shall allow presence of stabilizers in an amount of up to 3 wt.-% with respect the total weight of the inner layer and/or the presence of further

polymeric components in an amount of up to 3 wt.-% with respect the total weight of the inner layer as a matter of definition.

The polymer used for the skin layer can be a polypropylene homopolymer or a
5   random propylene ethylene copolymer, whereby the random propylene ethylene copolymer of the skin layer has an ethylene content of less than 2.5 wt.-%. Polypropylene homopolymers are preferred. It is further preferred that the polypropylene homopolymer has a melting temperature (Tm) of above 150°C, preferably above 154°C even more preferably above 162°C and most preferably
10   above 164°C. The melting temperature (Tm) upper limit is 170°C.

When a random propylene ethylene copolymer is present, the ethylene content is preferably 0.5 to 2.2 wt.-% and most preferably are 0.8 to 2.0 wt.-%. It is further preferred that the random propylene ethylene copolymer has a melting temperature
15   (Tm) in the range 145 – 160 °C more preferably 148 – 155 °C.

In a further aspect, the propylene homopolymer or the random propylene ethylene copolymer of the skin layer has an MFR (230°C, 2.16kg, ISO1133) of 2.0 to 20 g/10 min, preferably 3.0 to 15 g/10 min and most preferably 4.0 to 13 g/10min.
20

In yet a further aspect, the propylene homopolymer or the random propylene ethylene copolymer of the skin layer preferably has a flexural modulus of above 900 MPa more preferably above 950 MPa, most preferably above 975 MPa, when measured on injection molded specimens (23°C, 50% humidity, ISO 178). If a
25   propylene homopolymer is used, the flexural modulus is preferably above 1300 MPa, more preferably above 1450 MPa when measured on injection molded specimens (23°C, 50% humidity, ISO 178).

The styrene based thermoplastic elastomer (TPE) as used for the core layer has a
30   styrene content of from 5 to 20 wt.-%, preferably 5 to 15 wt.-% and more preferably 5 to 10 wt.-% and most preferably 5 to 9 wt.-%. The maximum of 20 wt.-% for the styrene content is highly important as the number average particle size of the TPO-TPE blend increases drastically above that value which in turn deteriorates haze properties.

The random heterophasic copolymer as used for the core layer is further preferably characterized by a melt flow rate (MFR) (ISO 1133; 230°C; 2.16kg) in the range of 0.5 to 20.0 g/10 min, preferably in the range of 1.0 to 15.0 g/10 min, more preferably in the range of 2.0 to 10.0 g/10 min, even more preferably in the range of 3.0 to 7.0 g/10 min and most preferably in the range of 3.5 to 6.5 g/10 min.

In a further aspect, the random heterophasic copolymer as used for the core layer preferably has a total ethylene comonomer content in the range of 5.0 to 16.0 wt%, preferably in the range of 6.0 to 15.0 wt% and more preferably in the range of 7.0 to 14.0 wt%.

The amount of the xylene cold soluble (XCS) fraction of the random heterophasic copolymer as used for the core layer preferably is in the range of 15.0 to 30.0 wt%, more preferably in the range of 18.0 to 30.0 wt% and most preferably in the range of 18.0 to 25.0 wt%.

The intrinsic viscosity (IV) measured according to ISO 1628-1 (at 135°C in decaline) of the XCS fraction of the random heterophasic copolymer as used for the core layer is in the range of more than 1.0 to 2.0 dl/g, preferably in the range of 1.1 to 1.8 dl/g and more preferably in the range of 1.2 to 1.6 dl/g.

In addition, the random heterophasic copolymer as used for the core layer has a melting temperature in the range of 130 °C to 145 °C. Preferably, the melting temperature of the random heterophasic copolymer as used for the core layer is in a range from 132 °C to below 144 °C, more preferably in the range from 134 °C to 143 °C.

The SSC random propylene ethylene copolymer as used for the inner layer has a melting temperature (Tm) from 120 °C to 144°C. It is further preferred the propylene ethylene copolymer as used for the inner layer has an ethylene content of 1.5 to 6.0 wt.-%, more preferably 1.6 to 4.0 wt.-%, most preferably 1.7 to 3.8 wt.-%.

- 12 -

In any case the melting temperature (Tm) of the SSC propylene ethylene copolymer of the inner layer must fulfil the following equation

$$Tm < 156 \text{ °C} - [5.2 \times C2 \text{ content in wt.-\%}] \text{ °C}$$

wherein C2 content stands for the content of units derived from ethylene;

Such melting temperature – content of units derived from ethylene is preferably obtained by the single site catalysts as described herein. However, other single site catalysts as known in the art can also be used.

In a preferred aspect, the melting temperature (Tm) of the SSC propylene ethylene copolymer of the inner layer fulfils the following equation

$$Tm < 154 \text{ °C} - [5.2 \times C2 \text{ content in wt.-\%}] \text{ °C}$$

wherein C2 content stands for the content of units derived from ethylene;

In a further aspect, the SSC propylene ethylene copolymer as used for the inner layer has an melt flow rate of 2.0 to 20 g/10min, more preferably 2.0 to 12.0 and most preferably 3.0 to 10.0 g/10min (230°C, 2.16kg, ISO1133).

In yet a further aspect, the SSC propylene ethylene copolymer as used for the inner layer preferably has a flexural modulus of from 500 to 1200 MPa, more preferably 500 to 1000 MPa and most preferably 600 to 900 MPa when measured on injection molded specimens (23°C, 50% humidity, ISO 178).

As mentioned above, the inner layer comprises, preferably consists of the single site catalyst derived (SSC) random propylene ethylene copolymer as described herein.

Alternatively but less preferred the inner layer comprises, preferably consists of a mixture obtainable by blending the single site catalyst derived (SSC) random propylene ethylene copolymer as described herein and a propylene ethylene elastomer having an ethylene content of less than 20 wt.-%. In yet a further alternative, the least one inner layer comprises, preferably consists of a mixture obtainable by blending the single site catalyst derived (SSC) random propylene

ethylene copolymer as described above and a styrene ethylene butylene styrene copolymer (SEBS).

In all three embodiments, the presence of stabilizers in an amount of up to 3 wt.-% and further polymeric components in an amount of up to 3 wt.-% both with respect to
5   the total weight of the inner layer shall be possible as a matter of definition. In other words, "consisting" as a matter of definition shall still allow presence of such minor amounts of stabilizers and polymeric components.

The present invention further provides a process for preparing the inventive
10   multilayer films.

The homo polypropylene or a random propylene ethylene copolymer having a MFR2 (ISO1133, 230°C) of 2 to 20g/10min and a melting temperature (Tm) of 145 °C to 170 °C for the skin layer and the random heterophasic copolymer for the core layer
15   are made with a catalyst system as described in the following.

The single site catalyst derived (SSC) random propylene ethylene copolymer having a melting temperature (Tm) from 120 °C to 144°C for the inner layer is made with a different catalyst namely a single site catalyst system. Single site catalysts provide a
20   different comonomer distribution being reflected by different melting temperature (Tm) – amounts of units derived from ethylene relation. Preferred single catalyst systems are described further below.

Thus, the present invention is preferably concerned with a multilayer film,
25   comprising at least a skin layer, a core layer and an inner layer,

the skin layer comprising a homo polypropylene or a random propylene ethylene copolymer including up to 2.5 wt.-% units derived from ethylene, the homopolypropylene or the random propylene ethylene copolymer having a MFR$_2$
30   (ISO1133, 230°C) of 2.0 to 20g/10min and a melting temperature (Tm) of 145 to 170°C, whereby the homo polypropylene or a random propylene ethylene copolymer is obtainable by polymerization in the presence of

    a)   a Ziegler-Natta catalyst (ZN-C) comprising compounds (TC) of a transition metal of Group 4 to 6 of IUPAC, a Group 2 metal compound (MC) and an internal donor (ID), wherein said internal donor (ID) is a selected from

- optionally substituted malonates,

5   - maleates,

- succinates,

- glutarates,

- cyclohexene-1,2-dicarboxylates,

- benzoates and derivatives and/or mixtures thereof,

10   - citraconate; or

- the combination of two internal donors (IDs) being 1,3-diethers and succinates

    b)   optionally a co-catalyst (Co), and

    c)   optionally an external donor (ED);

15

the core layer comprising a mixture obtainable by melt blending

20 to 80 wt.-% of a random heterophasic copolymer and 20 to 80 wt.-% of styrene based thermoplastic elastomer (TPE),

whereby the random heterophasic copolymer comprises a matrix phase and

20   dispersed therein an elastomer phase, whereby the matrix phase is formed by a random propylene ethylene copolymer and whereby the random heterophasic copolymer has a melting temperature (Tm) of 130 °C – 145 °C and includes an ethylene propylene copolymer rubber; and

whereby the styrene based thermoplastic elastomer (TPE) has a styrene

25   content of from 5 to 20 wt.-%,

whereby the random heterophasic copolymer is obtainable by polymerization in the presence of

    a)   a Ziegler-Natta catalyst (ZN-C) comprising compounds (TC) of a transition

30   metal of Group 4 to 6 of IUPAC, a Group 2 metal compound (MC) and an internal donor (ID), wherein said internal donor (ID) is a selected from

- optionally substituted malonates,

- maleates,

- succinates,

- glutarates,

- cyclohexene-1,2-dicarboxylates,

- benzoates and derivatives and/or mixtures thereof,

5   - citraconate

or

- the combination of two internal donors (IDs) being 1,3-diethers and
succinates

    b)   optionally a co-catalyst (Co), and
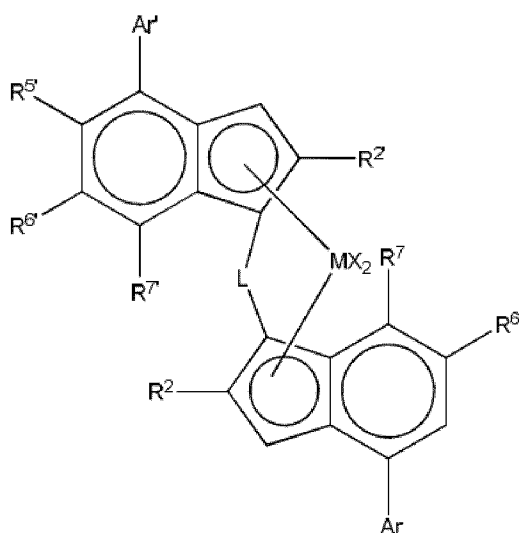
10   c)   optionally an external donor (ED);

and

the inner layer comprising a single site catalyst derived (SSC) random

15   propylene ethylene copolymer having a melting temperature (Tm) from 120
°C to 144°C, wherein further
the melting temperature (Tm) fulfils the following equation

$$Tm < 156\ °C - [5.2 \times C2\ \text{content in wt.-\%}]\ °C$$

20   wherein C2 content stands for the content of units derived from ethylene;

whereby the random propylene ethylene copolymer is obtainable by

polymerization in the presence of a single site catalyst comprising a complex

25   of formula (I)

wherein

M is zirconium or hafnium;

each X is a sigma ligand;

5   L is a divalent bridge selected from -R'2C-, -R'2C-CR'2-, -R'2Si-, -R'2Si-
           SiR'2-, -R'2Ge-, wherein each R' is independently a hydrogen atom, C1-C20-
           hydrocarbyl, tri(C1-C20-alkyl)silyl, C6-C20-aryl, C7-C20-arylalkyl or C7-C20-
           alkylaryl;

           R2 and R2' are each independently a C1-C20 hydrocarbyl radical optionally

10   containing one or more heteroatoms from groups 14-16;

           R5' is a C1-20 hydrocarbyl group containing one or more heteroatoms from
           groups 14-16,optionally substituted by one or more halo atoms;

           R6 and R6' are each independently hydrogen or a C1-20 hydrocarbyl group
           optionally containing one or more heteroatoms from groups 14-16; wherein

15   R6′ is preferably a tertiary alkyl group

           R7 is hydrogen or C1-20 hydrocarbyl group optionally containing one or
           more heteroatoms from groups 14-16;

           R7′ is hydrogen;

           Ar is independently an aryl or heteroaryl group having up to 20 carbon atoms

20   optionally substituted by one or more groups R1;

           Ar' is independently an aryl or heteroaryl group having up to 20 carbon
           atoms optionally substituted by one or more groups R1;

each R1 is a C1-20 hydrocarbyl group or two R1 groups on adjacent carbon
atoms taken together can form a fused 5 or 6 membered non aromatic ring
with the Ar group, said ring
 being itself optionally substituted with one or more groups R4;

5   each R4 is a C1-20 hydrocarbyl group;

and further a cocatalyst comprising at least one or two compounds of a
group 13 metal, e.g. Al and/or boron compound;

10

wherein the multilayer film is free of phthalic acid esters as well as
decomposition products thereof.

All preferred embodiments and aspects concerning the catalyst, catalyst system
15   and/or donor as described in the following shall also apply to the embodiment given
above.

The ZN catalyst as used for the present invention is

20   b)   a Ziegler-Natta catalyst (ZN-C) comprising compounds (TC) of a transition
              metal of Group 4 to 6 of IUPAC, a Group 2 metal compound (MC) and an
              internal donor (ID), wherein said internal donor (ID) is a selected from
              - optionally substituted malonates,
              - maleates,
25   - succinates,
              - glutarates,
              - cyclohexene-1,2-dicarboxylates,
              - benzoates and derivatives and/or mixtures thereof,
              - citraconate
30   or
              - the combination of two internal donors (IDs) being 1,3-diethers and
              succinates
       b)   optionally a co-catalyst (Co), and
       c)   optionally an external donor (ED).

Preferably, the internal donor (ID) is a citraconate and more preferably the molar-ratio of co-catalyst (Co) to external donor (ED) [Co/ED] is 5 to 45.

5   The Ziegler-Natta catalyst (ZN-C) can be further defined by the way as obtained. Accordingly, the Ziegler-Natta catalyst (ZN-C) is preferably obtained by a process comprising the steps of

a)

a_1)   providing a solution of at least a Group 2 metal alkoxy compound (Ax)
10   being the reaction product of a Group 2 metal compound (MC) and an
            alcohol (A) comprising in addition to the hydroxyl moiety at least one
            ether moiety optionally in an organic liquid reaction medium;

or

a_2)   a solution of at least a Group 2 metal alkoxy compound (Ax') being the
15   reaction product of a Group 2 metal compound (MC) and an alcohol
            mixture of the alcohol (A) and a monohydric alcohol (B) of formula
            ROH, optionally in an organic liquid reaction medium;

or

a_3)   providing a solution of a mixture of the Group 2 alkoxy compound (Ax)
20   and a Group 2 metal alkoxy compound (Bx) being the reaction product
            of a Group 2 metal compound (MC) and the monohydric alcohol (B),
            optionally in an organic liquid reaction medium; and

b)   adding said solution from step a) to at least one compound (TC) of a transition
     metal of Group 4 to 6 and

25   c)   obtaining the solid catalyst component particles,
     and adding a non-phthalic internal electron donor (ID) at any step prior to step c).

The internal donor (ID) or precursor thereof is added preferably to the solution of step a).

30

According to the procedure above the Ziegler-Natta catalyst (ZN-C) can be obtained via precipitation method or via emulsion (liquid/liquid two-phase system) –

solidification method depending on the physical conditions, especially temperature used in steps b) and c).

In both methods (precipitation or emulsion-solidification) the catalyst chemistry is the same.

In precipitation method combination of the solution of step a) with at least one transition metal compound (TC) in step b) is carried out and the whole reaction mixture is kept at least at 50 °C, more preferably in the temperature range of 55 to 110 °C, more preferably in the range of 70 to 100 °C, to secure full precipitation of the catalyst component in form of a solid particles (step c).

In emulsion - solidification method in step b) the solution of step a) is typically added to the at least one transition metal compound (TC) at a lower temperature, such as from -10 to below 50 °C, preferably from -5 to 30 °C. During agitation of the emulsion the temperature is typically kept at -10 to below 40 °C, preferably from -5 to 30 °C. Droplets of the dispersed phase of the emulsion form the active catalyst composition. Solidification (step c) of the droplets is suitably carried out by heating the emulsion to a temperature of 70 to 150 °C, preferably to 80 to 110 °C.

The catalyst prepared by emulsion - solidification method is preferably used in the present invention.

In a preferred embodiment in step a) the solution of a_2) or a_3) are used, i.e. a solution of (Ax') or a solution of a mixture of (Ax) and (Bx).

Preferably the Group 2 metal (MC) is magnesium.

The magnesium alkoxy compounds (Ax), (Ax') and (Bx) can be prepared *in situ in* the first step of the catalyst preparation process, step a), by reacting the magnesium compound with the alcohol(s) as described above, or said magnesium alkoxy compounds can be separately prepared magnesium alkoxy compounds or they can

be even commercially available as ready magnesium alkoxy compounds and used as such in the catalyst preparation process of the invention.

Illustrative examples of alcohols (A) are monoethers of dihydric alcohols (glycol monoethers). Preferred alcohols (A) are C_2 to C_4 glycol monoethers, wherein the ether moieties comprise from 2 to 18 carbon atoms, preferably from 4 to 13 carbon atoms. Preferred examples are 2-(2-ethylhexyloxy)ethanol, 2-butyloxy ethanol, 2-hexyloxy ethanol and 1,3-propylene-glycol-monobutyl ether, 3-butoxy-2-propanol, with 2-(2-ethylhexyloxy)ethanol and 1,3-propylene-glycol-monobutyl ether, 3-butoxy-2-propanol being particularly preferred.

Illustrative monohydric alcohols (B) are of formula ROH, with R being straight-chain or branched C_6-C_{10} alkyl residue. The most preferred monohydric alcohol is 2-ethyl-1-hexanol or octanol.

Preferably a mixture of Mg alkoxy compounds (Ax) and (Bx) or mixture of alcohols (A) and (B), respectively, are used and employed in a mole ratio of Bx:Ax or B:A from 8:1 to 2:1, more preferably 5:1 to 3:1.

Magnesium alkoxy compound may be a reaction product of alcohol(s), as defined above, and a magnesium compound selected from dialkyl magnesiums, alkyl magnesium alkoxides, magnesium dialkoxides, alkoxy magnesium halides and alkyl magnesium halides. Alkyl groups can be a similar or different C_1-C_{20} alkyl, preferably C_2-C_{10} alkyl. Typical alkyl-alkoxy magnesium compounds, when used, are ethyl magnesium butoxide, butyl magnesium pentoxide, octyl magnesium butoxide and octyl magnesium octoxide. Preferably the dialkyl magnesiums are used. Most preferred dialkyl magnesiums are butyl octyl magnesium or butyl ethyl magnesium.

It is also possible that magnesium compound can react in addition to the alcohol (A) and alcohol (B) also with a polyhydric alcohol (C) of formula R'' $(OH)_m$ to obtain said magnesium alkoxide compounds. Preferred polyhydric alcohols, if used, are alcohols, wherein R'' is a straight-chain, cyclic or branched C_2 to C_{10} hydrocarbon residue, and m is an integer of 2 to 6.

The magnesium alkoxy compounds of step a) are thus selected from the group consisting of magnesium dialkoxides, diaryloxy magnesiums, alkyloxy magnesium halides, aryloxy magnesium halides, alkyl magnesium alkoxides, aryl magnesium alkoxides and alkyl magnesium aryloxides. In addition a mixture of magnesium dihalide and a magnesium dialkoxide can be used.

The solvents to be employed for the preparation of the present catalyst may be selected among aromatic and aliphatic straight chain, branched and cyclic hydrocarbons with 5 to 20 carbon atoms, more preferably 5 to 12 carbon atoms, or mixtures thereof. Suitable solvents include benzene, toluene, cumene, xylene, pentane, hexane, heptane, octane and nonane. Hexanes and pentanes are particular preferred.

Mg compound is typically provided as a 10 to 50 wt-% solution in a solvent as indicated above. Typical commercially available Mg compound, especially dialkyl magnesium solutions are 20 – 40 wt-% solutions in toluene or heptanes.

The reaction for the preparation of the magnesium alkoxy compound may be carried out at a temperature of 40 °C to 70 °C. Most suitable temperature is selected depending on the Mg compound and alcohol(s) used.

The transition metal compound of Group 4 to 6 is preferably a titanium compound, most preferably a titanium halide, like $TiCl_4$.

The internal donor (ID) used in the preparation of the catalyst used in the present invention is preferably selected from substituted maleates and citraconates. Most preferably the internal donor is citraconate.

In emulsion method, the two phase liquid-liquid system may be formed by simple stirring and optionally adding (further) solvent(s) and additives, such as the turbulence minimizing agent (TMA) and/or the emulsifying agents and/or emulsion stabilizers, like surfactants, which are used in a manner known in the art for

- 22 -

facilitating the formation of and/or stabilize the emulsion. Preferably, surfactants are acrylic or methacrylic polymers. Particular preferred are unbranched C_{12} to C_{20} (meth)acrylates such as poly(hexadecyl)-methacrylate and poly(octadecyl)-methacrylate and mixtures thereof. Turbulence minimizing agent (TMA), if used, is

5   preferably selected from α-olefin polymers of α-olefin monomers with 6 to 20 carbon atoms, like polyoctene, polynonene, polydecene, polyundecene or polydodecene or mixtures thereof. Most preferable it is polydecene.

The solid particulate product obtained by precipitation or emulsion – solidification

10   method may be washed at least once, preferably at least twice, most preferably at least three times with aromatic and/or aliphatic hydrocarbons, preferably with toluene, heptane or pentane. The catalyst can further be dried, as by evaporation or flushing with nitrogen, or it can be slurried to an oily liquid without any drying step.

15   The finally obtained Ziegler-Natta catalyst is desirably in the form of particles having generally an average particle size range of 5 to 200 µm, preferably 10 to 100. Particles are compact with low porosity and have surface area below 20 g/m^2, more preferably below 10 g/m^2. Typically the amount of Ti is 1 to 6 wt-%, Mg 10 to 20 wt-% and donor 10 to 40 wt-% of the catalyst composition.

20

Detailed description of preparation of catalysts is disclosed in WO 2012/007430, EP 2 415 790, EP 2 610 270, EP 2 610 271 and EP 2 610 272 which are incorporated here by reference.

25   The Ziegler-Natta catalyst (ZN-C) is preferably used in association with an alkyl aluminum cocatalyst and optionally external donors.

As further component in the instant polymerization process an external donor (ED) is preferably present. Suitable external donors (ED) include certain silanes, ethers,

30   esters, amines, ketones, heterocyclic compounds and blends of these. It is especially preferred to use a silane. It is most preferred to use silanes of the general formula

$$R^a_p R^b_q Si(OR^c)_{(4-p-q)}$$
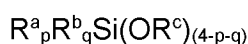
wherein R^a, R^b and R^c denote a hydrocarbon radical, in particular an alkyl or cycloalkyl group, and wherein p and q are numbers ranging from 0 to 3 with their sum p + q being equal to or less than 3. R^a, R^b and R^c can be chosen independently from one another and can be the same or different. Specific examples of such silanes are (tert-butyl)$_2$Si(OCH$_3$)$_2$, (cyclohexyl)(methyl)Si(OCH$_3$)^2, (phenyl)$_2$Si(OCH$_3$)$_2$ and (cyclopentyl)$_2$Si(OCH$_3$)$_2$, or of general formula

$$Si(OCH_2CH_3)_3(NR^3R^4)$$
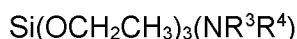
wherein R^3 and R^4 can be the same or different a represent a hydrocarbon group having 1 to 12 carbon atoms.

R^3 and R^4 are independently selected from the group consisting of linear aliphatic hydrocarbon group having 1 to 12 carbon atoms, branched aliphatic hydrocarbon group having 1 to 12 carbon atoms and cyclic aliphatic hydrocarbon group having 1 to 12 carbon atoms. It is in particular preferred that R^3 and R^4 are independently selected from the group consisting of methyl, ethyl, n-propyl, n-butyl, octyl, decanyl, iso-propyl, iso-butyl, iso-pentyl, tert.-butyl, tert.-amyl, neopentyl, cyclopentyl, cyclohexyl, methylcyclopentyl and cycloheptyl.

More preferably both R^1 and R^2 are the same, yet more preferably both R^3 and R^4 are an ethyl group.

Especially preferred external donors (ED) are the pentyl dimethoxy silane donor (D-donor) or the cyclohexylmethyl dimethoxy silane donor (C-Donor), the latter especially preferred.

In addition to the Ziegler-Natta catalyst (ZN-C) and the optional external donor (ED) a co-catalyst can be used. The co-catalyst is preferably a compound of group 13 of the periodic table (IUPAC), e.g. organo aluminum, such as an aluminum compound, like aluminum alkyl, aluminum halide or aluminum alkyl halide compound. Accordingly, in one specific embodiment the co-catalyst (Co) is a trialkylaluminium,

like triethylaluminium (TEAL), dialkyl aluminium chloride or alkyl aluminium dichloride or mixtures thereof. In one specific embodiment the co-catalyst (Co) is triethylaluminium (TEAL).

5   Advantageously, the triethyl aluminium (TEAL) has a hydride content, expressed as AlH_3, of less than 1.0 wt% with respect to the triethyl aluminium (TEAL). More preferably, the hydride content is less than 0.5 wt%, and most preferably the hydride content is less than 0.1 wt%.

10 Preferably the ratio between the co-catalyst (Co) and the external donor (ED) [Co/ED] and/or the ratio between the co-catalyst (Co) and the transition metal (TM) [Co/TM] should be carefully chosen.

Accordingly,

15 (a)   the mol-ratio of co-catalyst (Co) to external donor (ED) [Co/ED] preferably is in the range of 5 to 45, preferably is in the range of 5 to 35, more preferably is in the range of 5 to 25; and optionally

(b)   the mol-ratio of co-catalyst (Co) to titanium compound (TC) [Co/TC] preferably is in the range of above 80 to 500, preferably is in the range of 100 to

20 450, still more preferably is in the range of 120 to 350.

For the preparation of the homo polypropylene or the random propylene ethylene copolymer
for the skin layer having a MFR2 (ISO1133, 230°C) of 2 to 20g/10min and a melting

25 temperature (Tm) of 145 to 170 °C the external donor preferably is pentyl dimethoxy silane donor (D-donor) and the cocatalyst preferably is triethylaluminium (TEAL) and the weight ratio of cocatalyst triethylamluminium versus external donor pentyl dimethoxy silane donor (D-donor) preferably is in the range of 11/1 to 14/1, more preferably 12/1 to 13/1.

30

In a further aspect, the homo polypropylene or the random propylene ethylene copolymer for the skin layer is preferably made in a loop reactor.

For the preparation of the random heterophasic copolymer as used in the core layer the extrenal donor preferably is pentyl dimethoxy silane donor (D-donor) and the cocatalyst preferably is triethylaluminium (TEAL) and the weight ratio of cocatalyst triethylamluminium versus external donor pentyl dimethoxy silane donor (D-donor) preferably is in the range of 8/1 to 4/1, more preferably 7/1 to 5/1. In a further aspect, the random heterophasic copolymer is preferably prepared in coupled loop reactor – gas phase reactor 1 – gas phase reactor 2 setup. Further preferably the loop – gas phase reactor 1 are used for polymerization of the random propylene ethylene copolymer forming essentially the matrix.

The second catalyst, i.e. the single site catalyst as preferably used for the preparation of the single site catalyst derived (SSC) random propylene ethylene copolymer having a melting temperature (Tm) from 120 °C to 144°C, and wherein the melting temperature (Tm) fulfils the following equation

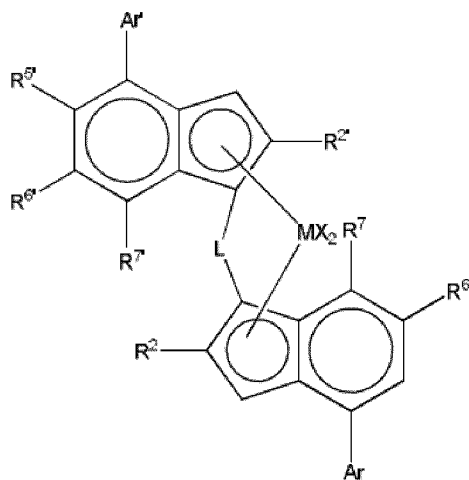$$Tm < 156 \ ^{\circ}C - [5.2 \times C2 \text{ content in wt.-\%}] \ ^{\circ}C$$

wherein C2 content stands for the content of units derived from ethylene;

as used for the inner layer is described below:

The polymerization of the single site catalyst derived (SSC) random propylene ethylene copolymer preferably takes place in the presence of a SSC catalyst comprising
(a) a complex of formula (I):

wherein

M is zirconium or hafnium;

each X is a sigma ligand;

5   L is a divalent bridge selected from -R'2C-, -R'2C-CR'2-, -R'2Si-, -R'2Si-SiR'2-, -
R'2Ge-,

wherein each R' is independently a hydrogen atom, C1-C20-hydrocarbyl, tri(C1-
C20- alkyl)silyl, C6-C20-aryl, C7-C20-arylalkyl or C7-C20-alkylaryl;

R2 and R2' are each independently a C1-C20 hydrocarbyl radical optionally

10   containing one or more heteroatoms from groups 14-16;

R5' is a C1-20 hydrocarbyl group containing one or more heteroatoms from groups
14-16

optionally substituted by one or more halo atoms;

R6 and R6' are each independently hydrogen or a C1-20 hydrocarbyl group

15   optionally containing one or more heteroatoms from groups 14-16; wherein R6´ is
preferably a tertiary alkyl group

R7 is hydrogen or C1-20 hydrocarbyl group optionally containing one or more
heteroatoms from groups 14-16;

R7´ is hydrogen;

20   Ar is independently an aryl or heteroaryl group having up to 20 carbon atoms
optionally substituted by one or more groups R1;

Ar' is independently an aryl or heteroaryl group having up to 20 carbon atoms
optionally substituted by one or more groups R1;

each R1 is a C1-20 hydrocarbyl group or two R1 groups on adjacent carbon atoms taken together can form a fused 5 or 6 membered non aromatic ring with the Ar group, said ring

being itself optionally substituted with one or more groups R4;

5   each R4 is a C1-20 hydrocarbyl group;
and

further a cocatalyst comprising at least one or two compounds of a group 13 metal, e.g. Al

10   and/or boron compound.

The catalyst used in the process of the invention is in solid particulate form. As mentioned above it can be supported on a conventional carrier know to an art skilled person. Preferably, the used catalyst is free from an external carrier.

15

Ideally, the catalyst is obtainable by a process in which
(a) a liquid/liquid emulsion system is formed, said liquid/liquid emulsion system comprising a solution of the catalyst components (i) and (ii) dispersed in a solvent so as to form dispersed droplets; and

20   (b) solid particles are formed by solidifying said dispersed droplets.

The term C1-20 hydrocarbyl group includes C1-20 alkyl, C2-20 alkenyl, C2-20 alkynyl, C3-20 cycloalkyl, C3-20 cycloalkenyl, C6-20 aryl groups, C7-20 alkylaryl groups or C7-20 arylalkyl groups or of course mixtures of these groups such as

25   cycloalkyl substituted by alkyl.

Unless otherwise stated, preferred C1-20 hydrocarbyl groups are C1-20 alkyl, C4-20 cycloalkyl, C5-20 cycloalkyl-alkyl groups, C7-20 alkylaryl groups, C7-20 arylalkyl groups or C6-20 aryl groups, especially C1-10 alkyl groups, C6-10 aryl groups, or

30   C7-12 arylalkyl groups, e.g. C1-8 alkyl groups.
Most especially preferred hydrocarbyl groups are methyl, ethyl, propyl, isopropyl, tertbutyl, isobutyl, C5-6-cycloalkyl, cyclohexylmethyl, phenyl or benzyl.
The term halo includes fluoro, chloro, bromo and iodo groups, especially chloro groups, when relating to the complex definition.

The oxidation state of the metal ion is governed primarily by the nature of the metal ion in question and the stability of the individual oxidation states of each metal ion. It will be appreciated that in the complexes of the invention, the metal ion M is

5   coordinated by ligands X so as to satisfy the valency of the metal ion and to fill its available coordination sites.

The nature of these σ-ligands can vary greatly.

Such catalysts are described in WO2013/007650, which is incorporated herein by

10   reference.

Thus, preferred complexes of use in the invention are of formula (II') or (II)

(II')   (II)
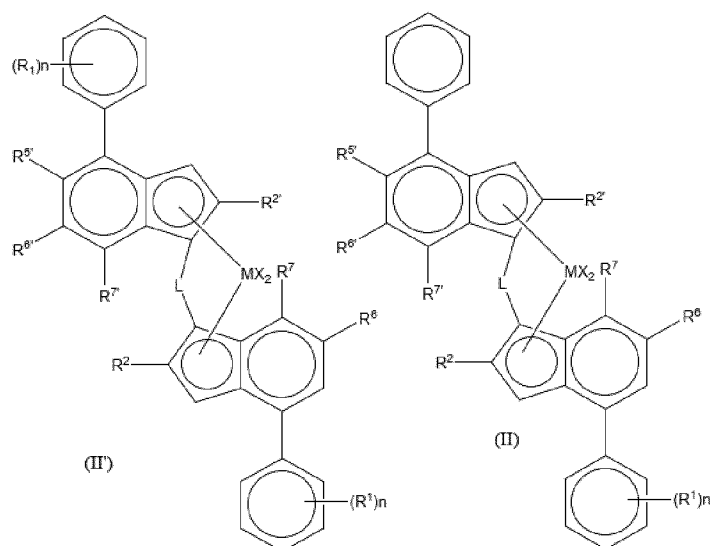
wherein

M is zirconium or hafnium;

15   each X is a sigma ligand, preferably each X is independently a hydrogen atom, a halogen

atom, C1-6 alkoxy group, C1-6 alkyl, phenyl or benzyl group;

L is a divalent bridge selected from -R'2C-, -R'2C-CR'2-, -R'2Si-, -R'2Si-SiR'2-, -R'2Ge-, wherein

20   each R' is independently a hydrogen atom, C1-20 alkyl, C3-10 cycloalkyl, tri(C1-20-alkyl)silyl, C6-20-aryl, C7-20 arylalkyl or C7-20 alkylaryl;

each R2 or R2' is a C1-10 alkyl group;

R5' is a C1-10 alkyl group or Z'R3' group;

R6 is hydrogen or a C1-10 alkyl group;

R6' is a C1-10 alkyl group or C6-10 aryl group; preferably a tertiary alkyl group;

R7 is hydrogen, a C1-6 alkyl group or ZR3 group;

R7' is hydrogen;

Z and Z' are independently O or S;

R3' is a C1-10 alkyl group, or a C6-10 aryl group optionally substituted by one or more halo groups;

R3 is a C1-10-alkyl group;

each n is independently 0 to 4, e.g. 0, 1 or 2;

and each R1 is independently a C1-20 hydrocarbyl group, e.g. C1-10 alkyl group.

Further preferred complexes of use in the invention are of formula (III') or (III):
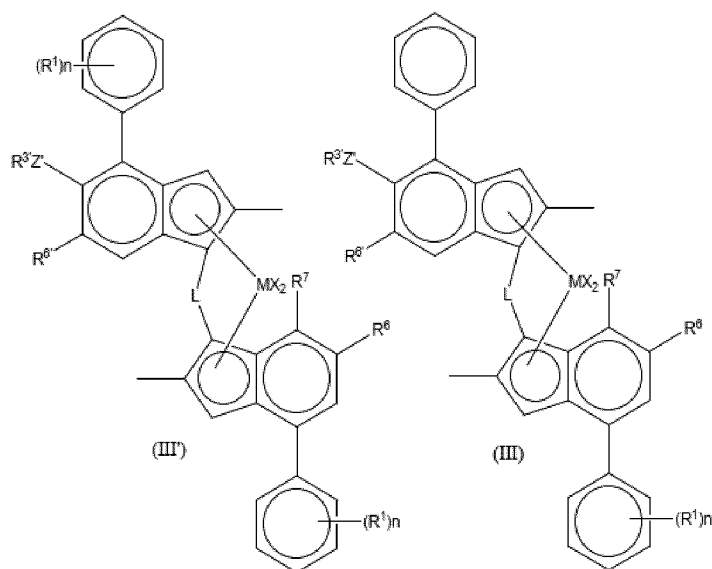
(III')   (III)

M is zirconium or hafnium;

each X is a sigma ligand, preferably each X is independently a hydrogen atom, a halogen

atom, C1-6 alkoxy group, C1-6 alkyl, phenyl or benzyl group;

L is a divalent bridge selected from -R'2C- or -R'2Si- wherein each R' is independently a

hydrogen atom, C1-20 alkyl or C3-10 cycloalkyl;

R6 is hydrogen or a C1-10 alkyl group;

5   R6' is a C1-10 alkyl group or C6-10 aryl group, preferably a tertiary alkyl group;

R7 is hydrogen, C1-6 alkyl or OC1-6 alkyl;

Z' is O or S;

R3' is a C1-10 alkyl group, or C6-10 aryl group optionally substituted by one or more halo groups;

10   n is independently 0 to 4, e.g. 0, 1 or 2; and each R1 is independently a C1-10 alkyl group.

Further preferred complexes of use in the invention are of formula (IV') or (IV):

(IV')   (IV)

15

M is zirconium or hafnium;

each X is a sigma ligand, preferably each X is independently a hydrogen atom, a halogen

20   atom, C1-6-alkoxy group, C1-6-alkyl, phenyl or benzyl group;

each R' is independently a hydrogen atom, C1-20 alkyl or C3-7 cycloalkyl;

R6 is hydrogen or a C1-10 alkyl group;

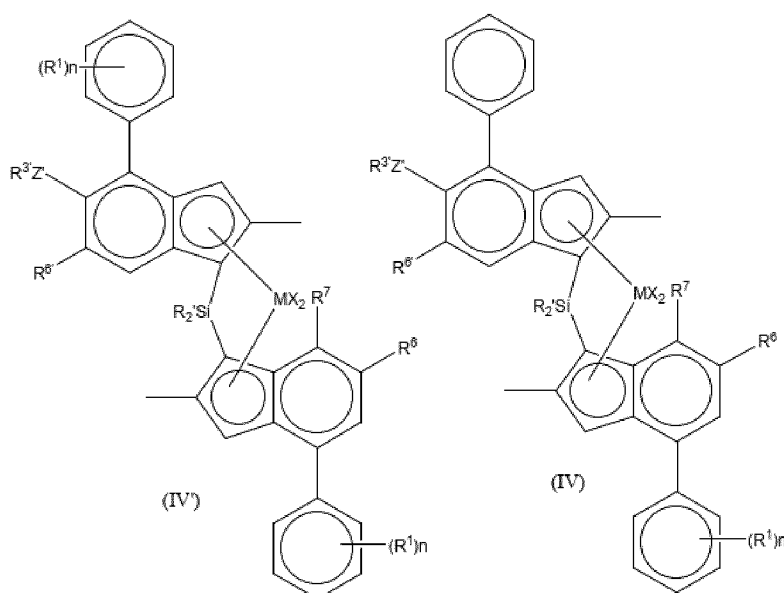R6' is a C1-10 alkyl group or C6-10 aryl group, preferably a tertiary alkyl group;

R7 is hydrogen, C1-6 alkyl or OC1-6 alkyl;

Z' is O or S;

R3' is a C1-10 alkyl group, or C6-10 aryl group optionally substituted by one or more

5   halo groups;

n is independently 0, 1 to 2; and

each R1 is independently a C3-8 alkyl group.

Most especially, the complex of use in the invention is of formula (V') or (V):

10

wherein each X is a sigma ligand, preferably each X is independently a hydrogen atom, a

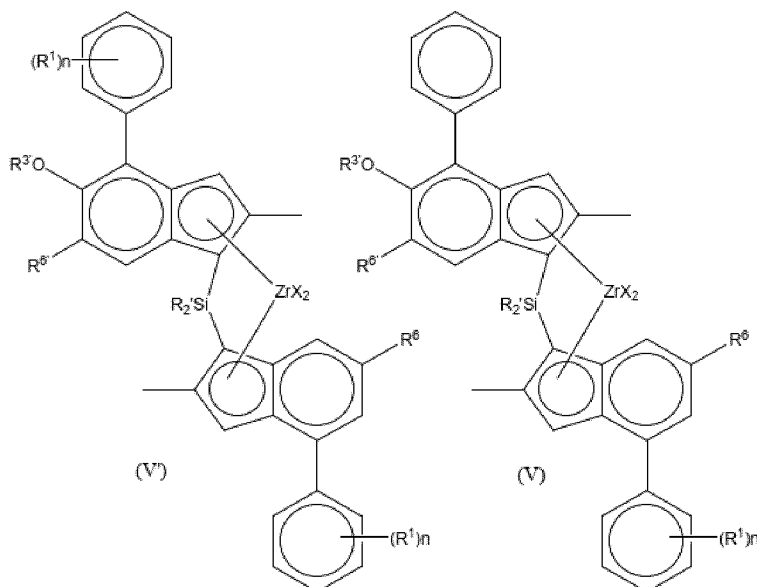halogen atom, C1-6-alkoxy group, C1-6-alkyl, phenyl or benzyl group;

15   R' is independently a C1-6 alkyl or C3-10 cycloalkyl;

R1 is independently C3-8 alkyl;

R6 is hydrogen or a C3-8 alkyl group;

R6' is a C3-8 alkyl group or C6-10 aryl group, preferably a tertiary C4-8 alkyl group;

R3' is a C1-6 alkyl group, or C6-10 aryl group optionally substituted by one or more

20   halo groups;

and

n is independently 0, 1 or 2.

Particular compounds of the invention include:

rac-anti-Me₂Si(2-Me-4-Ph-6-tBu-Ind)(2-Me-4-Ph-5-OMe-6-tBu-Ind)ZrCl₂	rac-anti-Me₂Si(2-Me-4-(p-tBuPh)-Ind)(2-Me-4-Ph-5-OMe-6-tBu-Ind)ZrCl₂	rac-anti-Me₂Si(2-Me-4-(3,5-di-tBuPh)-6-tBu-Ind)(2-Me-4-Ph-5-OMe-6-tBu-Ind)ZrCl₂	rac-anti-Me₂Si(2-Me-4-Ph-6-tBu-Ind)(2-Me-4,6-di-Ph-5-OMe-Ind)ZrCl₂

rac-anti-Me₂Si(2-Me-4-(p-tBuPh)-Ind)(2-Me-4-Ph-5-OC₆F₅)-6-iPr-Ind)ZrCl₂	rac-anti-Me(CyHex)Si(2-Me-4-Ph-6-tBu-Ind)(2-Me-4-Ph-5-OMe-6-tBu-Ind)ZrCl₂	rac-anti-Me₂Si(2-Me-4-(3,5-di-tBuPh)-7-Me-Ind)(2-Me-4-Ph-5-OMe-6-tBu-Ind)ZrCl₂	rac-anti-Me₂Si(2-Me-4-(3,5-di-tBuPh)-7-OMe-Ind)(2-Me-4-Ph-5-OMe-6-tBu-Ind)ZrCl₂

rac-anti-Me₂Si(2-Me-4-(p-tBuPh)-6-tBu-Ind)(2-Me-4-Ph-5-OMe-6-tBu-Ind)ZrCl₂	rac-anti-Me₂Si(2-Me-4-(p-tBuPh)-Ind)(2-Me-4-(4-tBuPh)-5-OMe-6-tBu-Ind)ZrCl₂	rac-anti-Me₂Si(2-Me-4-(p-tBuPh)-Ind)(2-Me-4-(3,5-tBu2Ph)-5-OMe-6-tBu-Ind)ZrCl₂	rac-anti-Me₂Si(2-Me-4-(p-tBuPh)-Ind)(2-Me-4-Ph-5-OiBu-6-tBu-Ind)ZrCl₂

Most preferably rac-anti-Me₂Si(2-Me-4-(p-tBuPh)-Ind)(2-Me-4-Ph-5-OMe-6-tBu-Ind)ZrCl₂ is used.

The synthesis of these materials is described in WO2013/007650.

Cocatalyst

To form an active catalytic species it is normally necessary to employ a cocatalyst
as is well known in the art. Cocatalysts comprising one or more compounds of
Group 13 metals, like organoaluminium compounds or borates or combinations
therefrom used to activate metallocene catalysts are suitable for use in this
invention. Thus, the cocatalyst is preferably an alumoxane, like MAO. As an
alternative borate cocatalysts can also be employed. It is also possible to use a
combination of an alumoxane and a borate cocatalyst.
 As borate cocatalyst, the use of B(C6F5)3, C6H5N(CH3)2H:B(C6F5)4,
(C6H5)3C:B(C6F5)4 or Ni(CN)4[B(C6F5)3]42- is especially preferred.
Further suitable cocatalysts are described in WO2013/007650.

Suitable amounts of cocatalyst will be well known to the person skilled in the art and
are for example disclosed in WO2015/11135.

The catalyst used to manufacture the C2C3 random copolymers of the invention is
ideally provided in solid particulate form but unsupported, i.e. no external carrier is
used. In order to provide the catalyst of the invention in solid form but without using
an external carrier, it is preferred if a liquid liquid emulsion system is used. The
process involves forming dispersing catalyst components (i) and (ii) in a solvent, and
solidifying said dispersed droplets to form solid particles.

In particular, the method involves preparing a solution of one or more catalyst
components; dispersing said solution in an solvent to form an emulsion in which said
one or more catalyst components are present in the droplets of the dispersed phase;
immobilising the catalyst components in the dispersed droplets, in the absence of an
external particulate porous support, to form solid particles comprising the said
catalyst, and optionally recovering said particles.

This process enables the manufacture of active catalyst particles with improved
morphology,

e.g. with a predetermined spherical shape and particle size and without using any added external porous support material, such as an inorganic oxide, e.g. silica. Also desirable surface properties can be obtained. WO2013/007650 again contains comprehensive details of this process.

Catalyst Prepolymerization

The use of the heterogeneous, non-supported catalysts, (i.e. "self-supported" catalysts) might have, as a drawback, a tendency to dissolve to some extent in the polymerization media, i.e. some active catalyst components might leach out of the catalyst particles during slurry polymerization, whereby the original good morphology of the catalyst might be lost. These leached catalyst components are very active possibly causing problems during polymerization. Therefore, the amount of leached components should be minimized, i.e. all catalyst components should be kept in heterogeneous form.

Furthermore, the self-supported catalysts generate, due to the high amount of catalytically active species in the catalyst system, high temperatures at the beginning of the polymerization which may cause melting of the product material. Both effects, i.e. the partial dissolving of the catalyst system and the heat generation, might cause fouling, sheeting and deterioration of the polymer material morphology.

In order to minimise the possible problems associated with high activity or leaching, it is preferred to "prepolymerize" the catalyst before using it in polymerization process. It has to be noted that prepolymerization in this regard is part of the catalyst preparation process, being a step carried out after a solid catalyst is formed. This catalyst prepolymerization step is not part of the actual polymerization configuration, which might comprise a conventional process prepolymerization step as well. After the catalyst prepolymerization step, a solid catalyst is obtained and used in polymerization.

Catalyst "prepolymerization" takes place following the solidification step of the liquid-liquid emulsion process hereinbefore described. Prepolymerization may take place by known methods described in the art, such as that described in WO 2010/052263,

WO 2010/052260 or WO 2010/052264. Preferable embodiments of this aspect of the invention are described herein.

5   As monomers in the catalyst prepolymerization step preferably alpha-olefins are used.
Preferable C2-C10 olefins, such as ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-heptene, 1-octene, 1-nonene 1-decene, styrene and vinylcyclohexene are used. Most preferred alpha-olefins are ethylene and propylene.

10

    The catalyst prepolymerization may be carried out in gas phase or in an inert diluent, typically oil or fluorinated hydrocarbon, preferably in fluorinated hydrocarbons or mixture of fluorinated hydrocarbons. Preferably perfluorinated hydrocarbons are used. The melting point of such (per)fluorinated hydrocarbons is
15   typically in the range of 0 to 140°C, preferably 30 to 120°C ,
like 50 to 110°C.

Where the catalyst prepolymerization is done in fluorinated hydrocarbons, the temperature for the prepolymerization step is below 70°C, e.g. in the range of -30 to
20   70°C, preferably 0-65°C and more preferably in the range 20 to 55°C.

Pressure within the prepolymerization vessel is preferably higher than atmospheric pressure to minimize the eventual leaching of air and/or moisture into the catalyst vessel. Preferably the pressure is in the range of at least 1 to 15 bar, preferably 2 to
25   10 bar. The prepolymerization vessel is preferably kept in an inert atmosphere, such as under nitrogen or argon or similar atmosphere.

Prepolymeriztaion is continued until the prepolymerization degree defined as weight of polymer matrix/weight of solid catalyst before prepolymerization step is reached.
30   The degree is below 25, preferably 0.5 to 10.0, more preferably 1.0 to 8.0, most preferably 2.0 to 6.0.

Use of the catalyst prepolymerization step offers the advantage of minimising leaching of catalyst components and thus local overheating.

After prepolymerization, the catalyst can be isolated and stored.

For the preparation of the single site catalyst derived (SSC) random propylene ethylene copolymer having a melting temperature (Tm) from 120 °C to 144°C and further the melting temperature (Tm) fulfilling the following equation

Tm < 156 °C – [5.2 x C2 content in wt.-%] °C

wherein C2 content stands for the content of units derived from ethylene; as used for the inner layer, a loop – gas phase reactor setup with a split of loop / gas phase of 40 to 60 versus 60 to 40 % (wt/wt) is used. It is particularly preferred to produce in the loop reactor an intermediate having essentially the same melt flow rate as the final random propylene ethylene copolymer.

The films according to the present invention are made on a multi layer case film line using at least 3 extruders.

The present invention is further concerned with pouches made from the multilayer film as described herein.

For the preparation of the homo polypropylene or the random propylene ethylene copolymer for the skin layer having a MFR2 (ISO1133, 230°C) of 2 to 20g/10min and a melting temperature (Tm) of 145 to 170°C the following combination (a) to (d) is preferably used:
   a) external donor: preferably dicyclopentyl dimethoxy silane donor (D-donor)
   b) cocatalyst: triethylaluminium (TEAL)
   c) weight ratio of cocatalyst (triethylaluminium) versus external donor (dicyclopentyl dimethoxy silane donor (D-donor)): in the range of 11/1 to 14/1, more preferably 12/1 to 13/1
   d) production in a loop reactor.

For the preparation of the random heterophasic copolymer as used in the core layer
the following combination (a) to (d) is preferably used:

a) extrenal donor: dicyclopentyl dimethoxy silane donor (D-donor)

b) cocatalyst: triethylaluminium (TEAL)

c) weight ratio of cocatalyst triethylamluminium versus external donor
    dicyclopentyl dimethoxy silane donor (D-donor): 8/1 to 4/1, preferably 7/1 to
    5/1

d) preparation in a coupled loop reactor – gas phase reactor 1 – gas phase
    reactor 2 setup, whereby the matrix is prepared in the loop – gas phase
    reactor 1.

Experimental Part

1.   Measuring methods

5   The following definitions of terms and determination methods apply for the above
general description of the invention as well as to the below examples unless
otherwise defined.

Phthalic acid esters and decomposition products Detection is carried out by
10   gas chromatography coupled with one- or two dimensional mass spectrometry (GC-
MS respectively GC-MS/MS) optionally preceded by enrichment on a suitable
adsorption material. "Free of phthalic acid esters as well as decomposition products
thereof" indicates
a maximum of 10 µg/kg, i.e. 10 ppb by weight. Typical equipment to be used is for
15   example given in H. Fromme, T. Küchler, T. Otto, K. Pilz, J. Müller, A. Wenzel
Water Research 36 (2002) 1429 – 1438 which is incorporated by reference
herewith.

Calculation of comonomer content of the second propylene copolymer fraction (R-
20   PP2):

$$\frac{C(PP) - w(PP1) x\, C(PP1)}{w(PP2)} = C(PP2) \quad (I)$$

wherein

w(PP1)   is the weight fraction [in wt.-%] of the first propylene copolymer
                fraction (R-PP1),

25   w(PP2)   is the weight fraction [in wt.-%] of second propylene copolymer
                fraction (R-PP2),

C(PP1)   is the comonomer content [in mol-%] of the first propylene copolymer
                fraction (R-PP1),

C(PP)   is the comonomer content [in mol-%] of the random propylene
30   copolymer (R-PP),

C(PP2)   is the calculated comonomer content [in mol-%] of the second
                propylene copolymer fraction (R-PP2).

Calculation of the xylene cold soluble (XCS) content of the second propylene copolymer fraction (R-PP2):

$$\frac{XS(PP) - w(PP1) \times XS(PP1)}{w(PP2)} = XS(PP2) \quad (II)$$

wherein

w(PP1)   is the weight fraction [in wt.-%] of the first propylene copolymer fraction (R-PP1),

w(PP2)   is the weight fraction [in wt.-%] of second propylene copolymer fraction (R-PP2),

XS(PP1)   is the xylene cold soluble (XCS) content [in wt.-%] of the first propylene copolymer fraction (R-PP1),

XS(PP)   is the xylene cold soluble (XCS) content [in wt.-%] of the random propylene copolymer (R-PP),

XS(PP2)   is the calculated xylene cold soluble (XCS) content [in wt.-%] of the second propylene copolymer fraction (R-PP2), respectively.

Calculation of melt flow rate MFR_2 (230 °C / 2.16 kg) of the second propylene copolymer fraction (R-PP2):

$$MFR(PP2) = 10^{\left[\frac{\log(MFR(PP)) - w(PP1) \times \log(MFR(PP1))}{w(PP2)}\right]} \quad (III)$$

wherein

w(PP1)   is the weight fraction [in wt.-%] of the first propylene copolymer fraction (R-PP1),

w(PP2)   is the weight fraction [in wt.-%] of second propylene copolymer fraction (R-PP2),

MFR(PP1)   is the melt flow rate MFR_2 (230 °C / 2.16 kg) [in g/10min] of the first propylene copolymer fraction (R-PP1),

MFR(PP)   is the melt flow rate MFR_2 (230 °C / 2.16 kg) [in g/10min] of the random propylene copolymer (R-PP),

MFR(PP2)   is the calculated melt flow rate MFR_2 (230 °C / 2.16 kg) [in g/10min] of the second propylene copolymer fraction (R-PP2).

Calculation of comonomer content of the elastomeric propylene copolymer (E), respectively:

$$\frac{C(RAHECO) - w(PP) x\, C(PP)}{w(E)} = C(E) \quad (IV)$$

wherein

5   w(PP)   is the weight fraction [in wt.-%] of the random propylene copolymer
                  (R-PP), i.e. polymer produced in the first and second reactor (R1 +
                  R2),

     w(E)   is the weight fraction [in wt.-%] of the elastomeric propylene
                  copolymer (E), i.e. polymer produced in the third reactor (R3)

10   C(PP)   is the comonomer content [in mol-%] of the random propylene
                  copolymer (R-PP), i.e. comonomer content [in mol-%] of the polymer
                  produced in the first and second reactor (R1 + R2),

     C(RAHECO)   is the comonomer content [in mol-%] of the propylene copolymer, i.e.
                  is the comonomer content [in mol-%] of the polymer obtained after
15   polymerization in the third reactor (R3),

     C(E)   is the calculated comonomer content [in mol-%] of elastomeric
                  propylene copolymer (E), i.e. of the polymer produced in the third
                  reactor (R3).

20   **MFR₂ (230 °C / 2.16 kg)** is measured according to ISO 1133 at 230 °C and 2.16 kg
     load.

     Quantification of microstructure by NMR spectroscopy

     Quantitative nuclear-magnetic resonance (NMR) spectroscopy was used to quantify
25   the comonomer content and comonomer sequence distribution of the polymers.
     Quantitative $^{13}C\{^1H\}$ NMR spectra were recorded in the solution-state using a Bruker
     Advance III 400 NMR spectrometer operating at 400.15 and 100.62 MHz for ^1H and
     ^{13}C respectively. All spectra were recorded using a ^{13}C optimised 10 mm extended
     temperature probehead at 125 °C using nitrogen gas for all pneumatics.
30   Approximately 200 mg of material was dissolved in 3 ml of $1,2$-tetrachloroethane-d_2
     (TCE-d_2) along with chromium-(III)-acetylacetonate (Cr(acac)₃) resulting in a 65 mM
     solution of relaxation agent in solvent (Singh, G., Kothari, A., Gupta, V., Polymer

Testing 28 5 (2009), 475). To ensure a homogenous solution, after initial sample preparation in a heat block, the NMR tube was further heated in a rotatary oven for at least 1 hour. Upon insertion into the magnet the tube was spun at 10 Hz. This setup was chosen primarily for the high resolution and quantitatively needed for

5   accurate ethylene content quantification. Standard single-pulse excitation was employed without NOE, using an optimised tip angle, 1 s recycle delay and a bi-level WALTZ16 decoupling scheme (Zhou, Z., Kuemmerle, R., Qiu, X., Redwine, D., Cong, R., Taha, A., Baugh, D. Winniford, B., J. Mag. Reson. 187 (2007) 225; Busico, V., Carbonniere, P., Cipullo, R., Pellecchia, R., Severn, J., Talarico, G.,

10   Macromol. Rapid Commun. 2007, 28, 1128). A total of 6144 (6k) transients were acquired per spectra.

Quantitative $^{13}C\{^1H\}$ NMR spectra were processed, integrated and relevant quantitative properties determined from the integrals using proprietary computer programs. All chemical shifts were indirectly referenced to the central methylene

15   group of the ethylene block (EEE) at 30.00 ppm using the chemical shift of the solvent. This approach allowed comparable referencing even when this structural unit was not present. Characteristic signals corresponding to the incorporation of ethylene were observed Cheng, H. N., Macromolecules 17 (1984), 1950).

With characteristic signals corresponding to 2,1 erythro regio defects observed (as

20   described in L. Resconi, L. Cavallo, A. Fait, F. Piemontesi, Chem. Rev. 2000, 100 (4), 1253, in Cheng, H. N., Macromolecules 1984, 17, 1950, and in W-J. Wang and S. Zhu, Macromolecules 2000, 33 1157) the correction for the influence of the regio defects on determined properties was required. Characteristic signals corresponding to other types of regio defects were not observed.

25   The comonomer fraction was quantified using the method of Wang et. al. (Wang, W-J., Zhu, S., Macromolecules 33 (2000), 1157) through integration of multiple signals across the whole spectral region in the $^{13}C\{^1H\}$ spectra. This method was chosen for its robust nature and ability to account for the presence of regio-defects when needed. Integral regions were slightly adjusted to increase applicability across the

30   whole range of encountered comonomer contents.

For systems where only isolated ethylene in PPEPP sequences was observed the method of Wang et. al. was modified to reduce the influence of non-zero integrals of sites that are known to not be present. This approach reduced the overestimation of

ethylene content for such systems and was achieved by reduction of the number of sites used to determine the absolute ethylene content to:

$$E = 0.5(S\beta\beta + S\beta\gamma + S\beta\delta + 0.5(S\alpha\beta + S\alpha\gamma))$$

Through the use of this set of sites the corresponding integral equation becomes:

5    $$E = 0.5(I_H + I_G + 0.5(I_C + I_D))$$

using the same notation used in the article of Wang et. al. (Wang, W-J., Zhu, S., Macromolecules 33 (2000), 1157). Equations used for absolute propylene content were not modified.

The mole percent comonomer incorporation was calculated from the mole fraction:

10   $$E\ [mol\%] = 100 * fE$$

The weight percent comonomer incorporation was calculated from the mole fraction:

$$E\ [wt\%] = 100 * (fE * 28.06) / ((fE * 28.06) + ((1-fE) * 42.08))$$

The comonomer sequence distribution at the triad level was determined using the analysis method of Kakugo et al. (Kakugo, M., Naito, Y., Mizunuma, K., Miyatake, T.

15   Macromolecules 15 (1982) 1150). This method was chosen for its robust nature and integration regions slightly adjusted to increase applicability to a wider range of comonomer contents.

The relative content of isolated to block ethylene incorporation was calculated from the triad sequence distribution using the following relationship (equation (I)):

20   $$I(E) = \frac{fPEP}{(fEEE + fPEE + fPEP)} \times 100 \qquad (I)$$

wherein

I(E) is the relative content of isolated to block ethylene sequences [in %];

fPEP is the mol fraction of propylene/ethylene/propylene sequences (PEP) in the sample;

25   fPEE is the mol fraction of propylene/ethylene/ethylene sequences (PEE) and of ethylene/ethylene/propylene sequences (EEP) in the sample;

fEEE is the mol fraction of ethylene/ethylene/ethylene sequences (EEE) in the sample.

30   **Intrinsic viscosity** is measured according to DIN ISO 1628/1, October 1999 (in Decalin at 135 °C).

The xylene cold solubles (XCS, wt.-%): Content of xylene cold solubles (XCS) is determined at 25 °C according ISO 16152; first edition; 2005-07-01. The part which remains insoluble is the xylene cold insoluble (XCI) fraction.

Melting temperature (T_m,) crystallization temperature (T_c) and heat of crystallization (H_c): measured with Mettler TA820 differential scanning calorimetry (DSC) on 5 to 10 mg samples. DSC is run according to ISO 11357-3:1999 in a heat / cool / heat cycle with a scan rate of 10 °C/min in the temperature range of +23 to +210 °C. The crystallization temperature is determined from the cooling step, while the melting temperature is determined from the second heating step.

Transparency, haze and clarity were determined according to ASTM D1003-00 on a 200 μmcast film as described herein.

Flexural Modulus: The flexural modulus was determined in 3-point-bending according to ISO 178 on 80x10x4 mm^3 test bars injection molded at 23 °C in line with EN ISO 1873-2.

Charpy notched impact strength is determined according to ISO 179 1eA at 23 °, and at
-20 °C by using an 80x10x4 mm^3 test bars injection molded in line with EN ISO 1873-2.

Tensile modulus in machine and transverse direction was determined according to ISO 527-3 at 23 °C on 200 μm cast films produced as described herein. . Testing was performed at a cross head speed of 1 mm/min.

Steam sterilization was performed in a Systec D series machine (Systec Inc., USA). The samples were heated up at a heating rate of 5 °C/min starting from 23 °C. After having been kept for 30 min at 121 °C, they were removed immediately from the steam sterilizer and stored at room temperature till processed further.

Sealing initiation temperature (SIT); (sealing end temperature (SET), sealing range)

The method determines the sealing temperature range (sealing range) of polypropylene films, in particular blown films or cast films. The sealing temperature range is the temperature range, in which the films can be sealed according to conditions given below. The lower limit (heat sealing initiation temperature (SIT)) is the sealing temperature at which a sealing strength of >3 N is achieved. The upper limit (sealing end temperature (SET)) is reached, when the films stick to the sealing device. The sealing range is determined on a J&B Universal Sealing Machine Type 3000 with a film of 50 μm thickness with the following further parameters:

Specimen width: 25.4 mm

Seal Pressure: 0.1 N/mm2

Seal Time: 0.1 sec

Cool time: 99 sec

Peel Speed: 10 mm/sec

Start temperature: 80 °C

End temperature: 150 °C

Increments: 10 °C

Specimen is sealed A to A at each sealbar temperature and seal strength (force) is determined at each step. The temperature is determined at which the seal strength reaches 3 N.

2.   Examples

Preparation of the phthalate free catalyst

The phthalate free catalyst used in the polymerization processes for the inventive resins (IE) was prepared as follows:

Used chemicals:

20 % solution in toluene of butyl ethyl magnesium (Mg(Bu)(Et), BEM), provided by Chemtura

2-ethylhexanol, provided by Amphochem

3-Butoxy-2-propanol - (DOWANOL™ PnB), provided by Dow

bis(2-ethylhexyl)citraconate, provided by SynphaBase

$TiCl_4$, provided by Millenium Chemicals

Toluene, provided by Aspokem

5   Viscoplex® 1-254, provided by Evonik

Heptane, provided by Chevron

Preparation of a Mg alkoxy compound

Mg alkoxide solution was prepared by adding, with stirring (70 rpm), into 11 kg of a

10   20 wt-% solution in toluene of butyl ethyl magnesium (Mg(Bu)(Et)), a mixture of 4.7

kg of 2-ethylhexanol and 1.2 kg of butoxypropanol in a 20 l stainless steel reactor.

During the addition the reactor contents were maintained below 45 °C. After addition

was completed, mixing (70 rpm) of the reaction mixture was continued at 60 °C for

30 minutes. After cooling to room temperature 2.3 kg g of the donor bis(2-

15   ethylhexyl)citraconate was added to the Mg-alkoxide solution keeping temperature

below 25 °C. Mixing was continued for 15 minutes under stirring (70 rpm).

Preparation of solid catalyst component

20.3 kg of $TiCl_4$ and 1.1 kg of toluene were added into a 20 l stainless steel reactor.

20   Under 350 rpm mixing and keeping the temperature at 0 °C, 14.5 kg of the Mg

alkoxy compound prepared in example 1 was added during 1.5 hours. 1.7 l of

Viscoplex® 1-254 and 7.5 kg of heptane were added and after 1 hour mixing at 0 °C

the temperature of the formed emulsion was raised to 90 °C within 1 hour. After 30

minutes mixing was stopped catalyst droplets were solidified and the formed catalyst

25   particles were allowed to settle. After settling (1 hour), the supernatant liquid was

siphoned away. Then the catalyst particles were washed with 45 kg of toluene at 90

°C for 20 minutes followed by two heptane washes (30 kg, 15 min). During the first

heptane wash the temperature was decreased to 50 °C and during the second wash

to room temperature.

30   The thus obtained catalyst was used along with triethyl-aluminium (TEAL) as co-

catalyst and dicyclopentyl dimethoxy silane (D-Donor) as donor.

The aluminium to donor ratio, the aluminium to titanium ratio and the polymerization

conditions are indicated in the respective tables

Preparation of the skin layer material

The polypropylene used for the skin layer material was prepared in a loop reactor using the catalyst as described above.

Table 1: Polymerization conditions used for preparation of the material for the skin layer.

Donor	dicyclopentyl dimethoxy silane
Teal/donor	12.5/1 (wt./wt.)
Teal/C3	0.15kg/ton
loop temperature	75°C
loop pressure	35Bar

The properties of the materials are shown in Table 2.

Table 2: Properties skin layer material

MFR (2.16kg, 230°C, ISO 1133)	8.0 g/10min
Tm (ISO 11357-3)	163 °C
Tcr (ISO 11357-3)	122
Flexural modulus (+23°C, ISO 178)	1350 MPa

Table 3: Preparation of the random heterophasic copolymer (RAHECO) for the core layer

		RAHECO for core layer inventive
Catalyst		as described above
Donor		dicyclopentyl dimethoxy silane
TEAL/Ti	[mol/mol]	220
TEAL/donor	[mol/mol]	6.1
Temperature	[°C]	31
Loop		
Temperature	[°C]	70
Split	[%]	33
H2/C3 ratio	[mol/kmol]	0.5
C2/C3 ratio	[mol/kmol]	5.7
MFR$_2$	[g/10min]	4

XCS	[wt.-%]	9.8
C2 content	[mol-%]	4.4
GPR 1		
Temperature	[°C]	80
Pressure	[kPa]	2500
Split	[%]	54
H2/C3 ratio	[mol/kmol]	7.8
C2/C3 ratio	[mol/kmol]	26.3
MFR$_2$	[g/10min]	6.3
XCS	[wt.-%]	8.1
C2 content	[mol-%]	6
GPR 2		
Temperature	[°C]	75
Split	[%]	13
C2/C3 ratio	[mol/kmol]	555
H2/C2 ratio	[mol/kmol]	502
MFR$_2$	[g/10min]	4.9
XCS	[wt.-%]	20.5
C2 content	[mol-%]	13.2
IV (XCS)	dl/g	1.3
Tm	°C	141

The polypropylenes powders were compounded with the desired amount of additves
(333ppm of Irganox 1010 (FF); 667ppm of Irgafos 168, 150ppm of Magnesium
oxide) in a ZSK 57 twin screw extruder with melt temperature of 200°C.

Preparation of core layer material:

The core layer material was made by compounding the RAHECO as obtained above
with 25.0 and 50.0 wt.-% of Kraton G1645MO based on the total amount of the core-
layer material in a ZSK 57 twin screw extruder with melt temperature of 200°C.

Kraton G1645MO is a linear triblock copolymer based on styrene and
ethylene/butylene (SEBS) having a melt flow rate (230°C, 2.16kg) of about 3
g/10min, a polystyrene content (KM 03 test method) of 11.5 to 13.5 wt.% measured
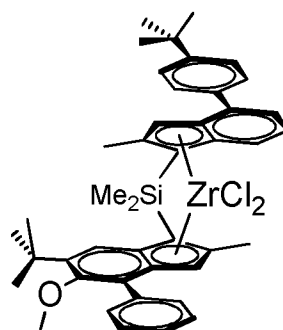on the polymer.

The random copolymer used in inner layer is made with a SSC catalyst as described in the following and the process parameters are shown in Table 5.

SSC catalyst

The metallocene D1 (rac-anti-dimethylsilandiyl(2-methyl-4-phenyl-5-methoxy-6-*tert*-butyl-indenyl)(2-methyl-4-(4-*tert*-butylphenyl)indenyl)zirconium dichloride) [shown below] was synthesized as described in WO 2013/007650.

The SSC-Catalyst was prepared using metallocene D1 and a catalyst system of MAO and trityl tetrakis(pentafluorophenyl)borate according to Catalyst 3 of WO 2015/11135 with the proviso that the surfactant was 2,3,3,3-tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)-1-propanol.

Table 5: Preparation of the SSC random heterophasic copolymer for the inner layer

		IE1	IE2
Catalyst		as described above	as described above
Loop			
Temperature	[°C]	70	70
Split	[%]	57	46
Feed H2/C3 ratio	[mol/kmol]	0.3	0.4
Feed C2/C3 ratio	[mol/kmol]	25.4	38.6
MFR$_2$	[g/10min]	8	7
XCS	[wt.-%]	n.m.	1.3
C2 content	[mol-%]	2	2.4
GPR 1			
Temperature	[°C]	80	80

Pressure	[kPa]	2500	2500
Split	[%]	43	54
H2/C3 ratio	[mol/kmol]	3.3	5.3
C2/C3 ratio	[mol/kmol]	117.8	178
MFR$_2$	[g/10min]	8	5
XCS	[wt.-%]	1.3	2.5
C2 content	[mol-%]	2.5	3.3

The polypropylenes powders were compounded with the desired amount of additives (333ppm of Irganox 1010 (FF); 667ppm of Irgafos 168, 500ppm of calcium stearate) in a ZSK 57 twin screw extruder with melt temperature of 200°C. The properties are shown in Table 6.

Table 4: Properties inner layer material

	CE1	IE1	IE2
Catalyst	ZN, citraconate donor	ssc as described above	ssc as described above
Phthalate free	yes	yes	yes
MFR (2.16kg, 230°C, ISO 1133) g/1min	8	8	5
C2 wt.-%	4.5	2.5	3.3
XS	8.5 wt.-%	nd	nd
Tm (ISO11357-3)	141 °C	140 °C	130 °C
Tm requirement according to claim 1 (for given C2)	Tm < 156°C – 5.2 x C2 (wt.-%) °C Tm < 156°C – (5.2 x 4.5)°C Tm < 133°C requirement not met	Tm < 156°C – 5.2 x C2 (wt.-%)°C Tm < 156°C – (5.2 x 2.5)°C Tm < 143°C requirement met	Tm < 156°C – 5.2 x C2 (wt.-%)°C Tm < 156°C – (5.2 x 3.3)°C Tm < 139°C requirement met

	Tm < 154°C – 5.2 x C2 (wt.-%) °C Tm < 131 °C	Tm < 154°C – 5.2 x C2 (wt.-%) °C Tm < 141°C	Tm < 154°C – 5.2 x C2 (wt.-%) °C Tm < 137°C
More specific Tm requirement	Not met	met	met

It can be seen a ZN catalyst such as the citraconate donor including ZN catalyst as used in the comparative example cannot provide the melting temperature – (content of units derived from ethylene)-relation.

5   The pelletization was done in a conventional way as well known in the art.

Preparation of the film

The films according to the present invention have been produced on a multi layer
10   cast film line equipped with 3 extruders. All three extruders were equipped with a notched feeding zone and a 3 zone screw with mixing and shear parts. The diameter of the cylinder of extruder A is 40 mm and the screw length 25D. Extruder B has a cylinder diameter of 60 mm and a screw length of SOD and extruder C a cylinder diameter of 45 mm and a screw length of 25D. Each extruder is fed by a
15   gravimetric dosing system. A feed block with lamellas and following distribution was used as co-extrusion adapter: Extruder A 10% (skin layer), extruder C 80% (core layer) and extruder B 10% (inner layer). A coat hanger die with automatic die gap regulation was used, die width 800 mm and die gap 0.5mm. The chill roll unit has a diameter of 450 mm and the 2nd cooling roll 250 mm. The detailed processing
20   parameters are shown in tables 6 below.

Table 5: processing conditions for three layer cast film

		Extruder A	Extruder C	Extruder B
Layer thickness	micron	20	160	20
Layer function and functionality		Skin layer Outer protection mainly vs. sterilization	Core layer	Inner layer sealing
Melttemperature	°C	250	260	250
Melt pressure	Bar	45	45	45
Screw speed	U/min	8	45	6
output	Kg/h	6	48	6
Coex adapter temperature		260		
Die temperature		250		
Chill roll temperature	°C	12		
2nd cooling roll temperature	°C	21		
Take off speed winder	m/min	7.4		

The core layer material was not varied, i.e. the amounts of Raheco and SEBS were 50 wt.-% Raheco and 50 wt.-% SEBS (Kraton G1645MO).

The comparative example was made with an inner layer made by the ZN catalyst as used for the core layer and the skin layer.

Table 6: Film properties determined on 200 μm films

...		IE1	IE2	CE1
SIT		122	113	123
Tensile Modulus/MD	MPa	157	159	155
Tensile Modulus/TD	MPa	135	138	130
Haze/b.s.	%	3.9	4.4	3.3
Haze/a.s.	%	7.0	7.0	9.1
clarity	%	98.7	98.2	96.9
free of phthalic acid esters / decomposition products		yes	yes	yes

5   b.s = before sterilization; a.s. = after sterilization

All inventive examples surprisingly showed improved haze after sterilization while tensile properties, haze before sterilization (less important) stayed on an excellent level. All inventive examples also surprisingly showed improved clarity. SIT was also
10 lower for the inventive examples.

It has been surprisingly found, that optical properties before and after sterilization can be significantly improved. Moreover, still some SIT improvement has been possible.
15

Claims

5   1.   Multilayer film comprising at least a skin layer, a core layer and an inner
         layer,

         the skin layer comprising a homo polypropylene or a random propylene
         ethylene copolymer including up to 2.5 wt.-% units derived from ethylene, the
10   homo polypropylene or the random propylene ethylene copolymer having a
         MFR_2 (ISO1133, 230°C) of 2.0 to 20g/10min and a melting temperature (Tm)
         of 145 to 170°C;

         the core layer comprising a mixture obtainable by melt blending
15   20 to 80 wt.-% of a random heterophasic copolymer and 20 to 80 wt.-% of
         styrene based thermoplastic elastomer (TPE),
         whereby the random heterophasic copolymer comprises
         -    a matrix phase and dispersed therein an elastomer phase, whereby the
              matrix phase is formed by a random propylene ethylene copolymer and
20   whereby the random heterophasic copolymer has
         -    a melting temperature (Tm) of 130 °C – 145 °C
         -    a flexural modulus of 250 to 850 MPa when measured on injection
              molded specimens (23°C, 50% humidity, ISO 178) and
         wherein the random heterophasic copolymer includes an ethylene propylene
25   copolymer rubber; and
         whereby the styrene based thermoplastic elastomer (TPE) has a styrene
         content of from 5 to 20 wt.-%, and

         the inner layer comprising a single site catalyst derived (SSC) random
30   propylene ethylene copolymer having
         -    a melting temperature (Tm) from 120°C to 144°C,
         -    a content of units derived from ethylene in an amount of 1.5 to 6.0 wt.-%,
         -    the melting temperature (Tm) fulfilling the following equation

Tm < 156 °C – [5.2 x C2 content in wt.-%] °C

wherein C2 content stands for the content of units derived from ethylene; and

- a xylene cold soluble content (ISO 16152, 1st ED, 2005-07-01; 25°C) of preferably below 30 wt.-%

wherein the multilayer film is free of phthalic acid esters as well as decomposition products thereof.
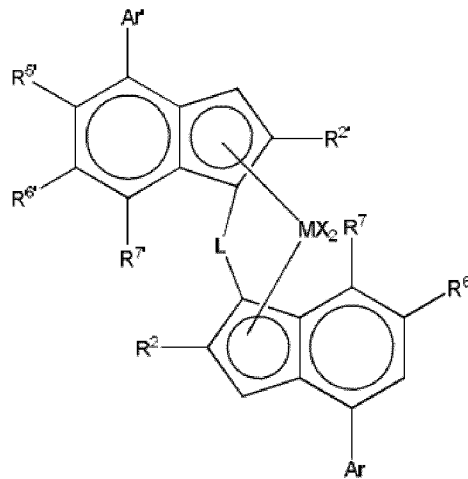
2.   Multilayer film according to claim 1, whereby xylene cold soluble fraction (XCS) of the random heterophasic copolymer contributing to the core layer has an intrinsic viscosity of 1.0 to 2.0 dl/g (DIN ISO 1628/1, 10/1999; Decalin, 135°C).

3.   Multilayer film according to claim 1 or 2 has a total thickness of 50 to 250 micrometer.

4.   Multilayer film according to any of the preceding claims, whereby the core layer has a thickness of 50 to 85 % with respect to the thickness of the multilayer film.

5.   Multilayer film according to any of the preceding claims, whereby the thicknesses of the skin layer is 10 to 25% with respect to the total thickness of the multilayer film

and/or

and whereby

the thicknesses of the inner layer is 10 to 25 % with respect to the total thickness of the multilayer film.

6.   Multilayer film according to any of the preceding claims, whereby the skin layer consists of the homo polypropylene or random propylene ethylene copolymer;

and/or

the core layer consists of the mixture obtainable by melt blending

20 to 80 wt.-% of a random heterophasic copolymer and 20 to 80 wt.-% of

styrene based thermoplastic elastomer (TPE);

and/or

the inner layer consists of the single site catalyst derived (SSC) random

propylene ethylene copolymer,

or

the inner layer consists consists of

a mixture obtainable by blending the single site catalyst derived (SSC)

random propylene ethylene copolymer and a propylene ethylene elastomer

having an ethylene content of less than 20 wt.-%;

or the inner layer consists of

a mixture obtainable by blending the single site catalyst derived (SSC)

random propylene ethylene copolymer and a styrene ethylene butylene

styrene copolymer (SEBS).

7.   Multilayer film according to any of the preceding claims,

whereby the propylene homopolymer of the skin layer has an MFR (230°C,

2.16kg, ISO1133) of 4.0 to 13g/10min

and/or

a melting temperature of above 154°C up to 170°C

and/or

a flexural modulus of above 1300 MPa when measured on injection molded

specimens (23°C, 50% humidity, ISO 178).

or

the random propylene ethylene copolymer of the skin layer has

an MFR (230°C, 2.16kg, ISO1133) of 4.0 to 13 g/10min

an ethylene content of 0.5 to 2.2 wt.-%

and/or

a melting temperature of 145 to 155 °C

and/or

a flexural modulus of above 975 MPa when measured on injection molded

specimens (23°C, 50% humidity, ISO 178).

- 56 -

8.   Multilayer film according to according to any of the preceding claims, whereby the random heterophasic copolymer having a melting temperature (Tm) of 130 to 145 °C contributing to the core layer has

a MFR$_2$ of 3.0 to 7.0 g/10min (ISO 1133, 230°C, 2.16 kg)

and/or

a total ethylene content of 7.0 to 14.0 wt.-%

and/or

an amount of the xylene cold soluble fraction (XCS) in the range of 18.0 to 25.0 wt.-%

and/or

an intrinsic viscosity of 1.0 to 1.6 dl/g (DIN ISO 1628/1, 10/1999; Decalin, 135°C) of the xylene cold soluble fraction (XCS).

9.   Multilayer film according to any of the preceding claims, whereby the single site catalyst derived (SSC) random propylene ethylene copolymer of the inner layer has a the melting temperature (Tm) fulfilling the following equation

Tm < 154 °C – [5.2 x C2 content in wt.-%] °C

wherein C2 content stands for the content of units derived from ethylene; ,

and/or

has an ethylene content of 1.5 to 6.0 wt.-%, preferably 1.6 to 4.0

and/or

has an melt flow rate of 3.0 to 20 preferably 3.0 to 9.0 g/10min (230°C, 2.16kg, ISO1133),

and/or

a flexural modulus of from 600 to 900 MPa when measured on injection molded specimens (23°C, 50% humidity, ISO 178).

10.   Multilayer film according to any of the preceding claims, whereby the core layer layer comprises a mixture obtainable by melt blending 40 to 60wt.-% of a random heterophasic copolymer and 60 to 40 wt.-% of styrene based thermoplastic elastomer (TPE).

11.   Multilayer film according to any of claims 1 to 9,
      whereby the core layer layer comprises a mixture obtainable by melt
      blending 60 to 80 wt.-% of a random heterophasic copolymer and 40 to 20
      wt.-% of styrene based thermoplastic elastomer (TPE).

12.   Pouches made from the multilayer film as defined in any of claims 1 to 11.

13.   Process for preparing a film according to any of claims 1 to 12, whereby the
      components forming the skin layer, the core layer and the inner layer are
      extruded on a multi layer cast film line.

14.   Process for preparing a film according to any of claims 1 to 12, wherein the
      single site catalyst derived (SSC) random propylene ethylene copolymer is
      obtained in the presences of a single site catalysts comprising
      (i) a complex of formula (I):

wherein
M is zirconium or hafnium;
each X is a sigma ligand;
L is a divalent bridge selected from -R'2C-, -R'2C-CR'2-, -R'2Si-, -R'2Si-
SiR'2-, -R'2Ge-,
wherein each R' is independently a hydrogen atom, C1-C20-hydrocarbyl,
tri(C1-C20-
alkyl)silyl, C6-C20-aryl, C7-C20-arylalkyl or C7-C20-alkylaryl;

R2 and R2' are each independently a C1-C20 hydrocarbyl radical optionally containing one

or more heteroatoms from groups 14-16;

R5' is a C1-20 hydrocarbyl group containing one or more heteroatoms from groups

5   14-16

optionally substituted by one or more halo atoms;

R6 and R6' are each independently hydrogen or a C1-20 hydrocarbyl group optionally

containing one or more heteroatoms from groups 14-16; wherein R6´ is preferably a

10   tertiary

alkyl group

R7 is hydrogen or C1-20 hydrocarbyl group optionally containing one or more heteroatoms

from groups 14-16;

15   R7´ is hydrogen;

Ar is independently an aryl or heteroaryl group having up to 20 carbon atoms optionally

substituted by one or more groups R1;

Ar' is independently an aryl or heteroaryl group having up to 20 carbon atoms

20   optionally

substituted by one or more groups R1;

each R1 is a C1-20 hydrocarbyl group or two R1 groups on adjacent carbon atoms taken

together can form a fused 5 or 6 membered non aromatic ring with the Ar group,

25   said ring

being itself optionally substituted with one or more groups R4;

each R4 is a C1-20 hydrocarbyl group;

and

30

(ii) a cocatalyst comprising at least one or two compounds of a group 13 metal, e.g. Al and/or boron compound.

15.   Process for preparing a film according to any of claims 1 to 12,

comprising at least a skin layer, a core layer and an inner layer, wherein the the skin layer comprises a homo polypropylene or a random propylene ethylene copolymer including up to 2.5 wt.-% units derived from ethylene, the homopolypropylene or the random propylene ethylene copolymer having a MFR_2

5 (ISO1133, 230°C) of 2.0 to 20g/10min and a melting temperature (Tm) of 145 to 170°C, whereby the homo polypropylene or the random propylene ethylene copolymer is obtainable by polymerization in the presence of

a Ziegler-Natta catalyst (ZN-C) comprising compounds (TC) of a transition metal of

10 Group 4 to 6 of IUPAC, a Group 2 metal compound (MC) and an internal donor (ID), wherein said internal donor (ID) is a selected from

- optionally substituted malonates,
- maleates,
- succinates,

15 - glutarates,
- cyclohexene-1,2-dicarboxylates,
- benzoates and derivatives and/or mixtures thereof,
- citraconate; or
- the combination of two internal donors (IDs) being 1,3-diethers and

20 succinates

b) optionally a co-catalyst (Co), and

c) optionally an external donor (ED);

25