Polymer composition comprising a cyclic olefin polymer (COP) and a syndiotactic PP (s-PP) is described. A film including a layer comprising such a composition and specific applications thereof is also described.
POLYMER COMPOSITION INCLUDING A CYCLIC OLEFIN COPOLYMER

[0001] The present invention relates to a polymer composition including a cyclic olefin copolymer, to a film including a layer consisting of this composition and to specific applications thereof.

[0002] Articles intended for medical applications must meet not only conventional requirements, such as good mechanical strength or low cost, but also requirements—extremely strict—peculiar to this specific field of application, such as, for example, requirements relating to the biocompatibility properties of the said articles, their ability to be subjected to a sterilization treatment, their flexibility, their transparency, their weldability, their impact strength (including as regards containers filled with liquid), the amount of extractable substances (for example, with hexane) and in some cases, their barrier properties.

[0003] Until now, commercially available articles for medical use, for example infusion or blood bags, and bags intended for the conservation of medical related fluids, have been based on vinyl chloride polymers, for example on PVC. Although having several advantages, this type of polymer, however, has certain disadvantages, such as the need to incorporate high amounts of stabilizers therein for the purpose of improving its thermal stability or to incorporate high amounts of plasticizers therein for the purpose of obtaining sufficient flexibility. There is therefore a market demand for articles for medical applications which are devoid of chlorinated polymers.

[0004] To get such articles, it is known to start from polyolefin-based films and to weld these together (or on themselves) in order to make bags or pouches. Patent application WO 00/61062 in the name of SOLVAY describes such films which may comprise a COP (cyclic olefin polymer). However, the applicant found that when a COP is used alone (i.e. as a pure constituent of a film or a layer therefrom), welding is very uneasy and the welds obtained are of poor quality, especially with the short welding times commonly used in industrial processes. Besides, heat sterilisation, transparency and flexibility are not optimal when using pure COP, even in only one layer of a multilayer structure. More particularly, multilayer structures including a pure COP layer tend to delaminate after heat sterilisation.

[0005] The applicant found that surprisingly, when adding a syndiotactic polypropylene (s-PP) to a COP, the latter becomes very easy to weld and allows to make medical bags or pouches which can be heat sterilised, are and remain (after sterilisation) transparent, flexible, have a high impact strength and besides, show excellent barrier properties (namely against water vapour, acids and alcohols) and no delamination after heat sterilisation in the case of a multilayer structure. Besides, s-PP is obtained through metallocene catalysts, so it shows a low amount of extractable compounds and less catalytic residues than other non-metallocene PP resins.

[0006] Accordingly, the present invention relates to a polymer composition comprising a COP and a s-PP.

[0007] The term “COP” is understood to mean a homo- or a copolymer of a C5 to C12 cyclic monomer and/or di-cyclic monomer (dimer), which may bear side chains so as to reach a total of 5 to 30 C. Copolymers generally include besides the cyclic monomer, a C2 to C10 olefin in a respective content of 2 to 95% (preferably 10 to 80%) by weight for the cyclic monomer and 5 to 98% (preferably 20 to 90%) by weight for the olefin. The basic cyclic monomer unit can be cyclopentene, cyclohexene, norbornene, dicyclopentadiene, tetra cyclicododecene or methyltetra cyclicododecene. It is preferably norbornene:

[0008] eventually bearing side chains which may be linear:

[0009] R1, R2 (=CxHy+1 with x,y=0, 1, 2, . . . )

[0010] or cyclic, like in dicyclopentadiene (which is in fact norbornene with a cyclopentadiene side chain):

[0011] The olefin is advantageously ethylene. The COP is preferably a homo- or copolymer of norbornene with or without side chains; it is more preferably either a homopolymer of norbornene (with or without side chains, but preferably with cyclopentadiene as side chain, i.e. it is preferably a homopolymer of dicyclopentadiene), or a copolymer of norbornene (with or without side chains) and ethylene. In the latter case, the content of ethylene is advantageously between 30 and 95% (preferably between 40 and 80%) by weight and the content of norbornene between 5 and 70% (preferably between 20 and 60%).

[0012] The s-PP according to the present invention may be a homopolymer or a copolymer of propylene with up to 30% of a C2-C4 monomer, preferably ethylene. It preferably is a polyolefin of controlled crystallinity as described in WO 00/61062. It preferably shows a softening point (or “Vicat point”) of less than 121° C. (measured according to ASTM Standard D1525), at least after having been processed in appropriate conditions (which are described in WO 00/61062, incorporated herein by reference), even if the producer of the resin announces higher values. The s-PP according to the present invention thus preferably exhibit the distinguishing feature that their crystallinity can be easily reduced during their processing. This ready control of the
crystallinity is advantageous in the content of the invention, in so far as it makes it possible to confer a reduced crystallinity on these s-PP resins, provided that appropriate processing conditions are used, thus increasing the transparency and the flexibility of the whole structure.

[0013] The polydispersity of the s-PP according to the present invention is advantageously less than 8 and preferably less than 4. This characteristic reflects a low dispersion of the molecular masses, which increases the separation between the melting temperature ranges and softening temperature ranges and thus makes it possible to have a more effective action on the crystallinity during the processing.

[0014] Furthermore, the melt flow index of the s-PP used is advantageously less than 10 g/10 min, preferably less than 6 g/10 min (measured according to ASTM Standard D1238, under the conditions 190°C/2.16 kg for the polymers of ethylene and the copolymers of butene and under the conditions 230°C/2.16 kg for the polymers of propylene and the homopolymers of butene).

[0015] In the composition according to the present invention, the s-PP is generally present in an amount of 1% or more, or even 10% or more (in weight compared with the total weight of the blend), while the COP content of the blend is generally of 70% or more, or even 80% or more. Generally, the s-PP is present in amount of 30% or less, or even 20% or less, while the COP is present in amount of 99% or less, or even 90% or less.

[0016] In addition to the s-PP and the COP resin, the composition according to the present invention may comprise other thermoplastic polymers. These other polymers are advantageously chosen from not very crystalline or amorphous polyolefins or hydrocarbons of the following types:

[0017] olefinic copolymers composed of at least two C₂ to C₁₀ alkenes, comprising at least 60% by weight of ethylene and/or of propylene and/or of butene but not comprising more than 90% by weight of the same comonomer, or from

[0018] olefinic copolymers comprising ethylene and/or propylene and/or butene and from 10 to 40% by weight of one or more different comonomers which are preferably chosen from C₂ to C₁₀ olefins (for instance copolymers of ethylene and 1-octene in an amount such to have linear low density polyethylene (LLDPE), very low density polyethylene (VLDPE) or ultra low density polyethylene (ULDPE) and carbonylic acid or ester groups, for example vinyl acetate, methyl ethyl or butyl acrylate and methyl methacrylate, or carbon monoxide, or from

[0019] elastomeric copolymers with blocks of styrene and of an olefin (for example, copolymers of the styrene-butadiene-styrene, styrene-ethylene-butylene-styrene or styrene-ethylene-propylene-styrene type, and the like), or from

[0020] highly branched homopolymers [for example, low density polyethylene (LDPE) or medium density polyethylene (MDPE)]

[0021] hydrogenated hydrocarbons like paraffin or paraffinic oil.

[0022] Advantageously, the composition according to the present invention additionally comprises at least one resin chosen between styrene-ethylene-butylene-styrene (SEBS), eventually including styrene-ethylene-butylene (SEB), styrene-ethylene-propylene-styrene (SEPS), eventually including styrene-ethylene-propylene (SEP), and ethylene-1-octene copolymers (preferably made by metallocene technology). SEBS and/or SEPS are preferred because they allow to make both permanent seals and peelable seals (at a lower temperature) with the film and because their impact strength. The total concentration of these resins is generally equal to or higher than 1% (in weight with relation to the entire composition), and preferably equal to or higher than 10%. It is generally equal to or lower than 29%, preferably 20%.

[0023] The composition according to the present invention may easily be processed in any kind of object, from a flat one (like a film or sheet) to a three dimensional one (like a container), and either into a monolayer structure or into a multilayer one.

[0024] In one preferred embodiment, the present invention relates to a film comprising at least one basic layer including the above described composition.

[0025] The term “film” is used to denote a thin, flat structure or a tubular one (in the case of blown films) which generally has a thickness of 1000 µm or less, preferably 500 µm or less, or even 250 µm or less. In practice, a thickness of 100 µm or more is suitable, or even 150 µm or more.

[0026] The film according to the present invention generally has at least one other layer besides the basic one comprising the composition based on s-PP and COP. Since COPs are sensitive to grease, even in low amounts such as when touching or manipulating it, the film according to the present invention preferably comprises at least one external layer which does not comprise a COP, and preferably even two such external layers. In that case, these layers are positioned on each side of the basic layer. The additional layer(s) preferably comprise at least 30% of metallocene technology PP (either syndiotactic or isotactic, either homo- or copolymer, for instance with ethylene). The choice of PP resins obtained through metallocene catalyst technology, improves the purity (content of extractibles and catalytic residues) of the entire structure. According to a preferred embodiment of the present invention, the film comprises at least on one side of the basic layer, a layer comprising s-PP and/or i-PP made by metallocene technology and at least one resin chosen between SEBS, SEBS with SEB, SEPS, SEPS with SEP and ethylene-1-octene copolymers made by metallocene technology, for the same reason as explained above. The total concentration of these resins is generally equal to or lower than 70%.

[0027] In order to further improve the scalability of the film according to the invention, it is advantageous that it comprises at least one outer layer (the sealing layer) comprising s-PP and/or i-PP made by metallocene technology; at least one resin chosen between SEBS, SEBS with SEB, SEPS, SEPS with SEP and ethylene-1-octene copolymers made by metallocene technology; and at least one not very crystalline or amorphous polyolefin chosen between ethylene-vinyl acetate (EVA), ethylene-methyl acrylate (EMA), ethylene-ethyl acrylate (EEA) or ethylene-butyl acrylate (EBA) copolymers. Among the last mentioned copolymers,
only those which exhibit a content of comonomer(s) of at least 10% naturally come into consideration as additional constituents. The concentration of these copolymers is generally equal to or higher than 0.1% (in weight with relation to the entire composition), and preferably than 1%. It is generally equal to or lower than 15%, preferably lower than 10% and most preferably lower than 7%. A mixture of EVA and EMA, preferably in a total amount of at least 1%, or even at least 5%, gives good results. It makes it namely possible to make welds with very reproducible peel strengths, which is very useful for making items with a pealable seal, like multi-chamber bags or pouches including a permanent, outer seal and at least one pealable seal.

[0028] Besides the layers mentioned above, it may be of interest from an economical point of view, to include a layer made of scraps (of films according to the present invention), as internal layer in the films described above.

[0029] The film according to the present invention may be embossed (i.e. may carry a pattern in relief) by any known technique in order to prevent blocking.

[0030] The film according to the present invention may additionally include a barrier layer comprising a resin like EVOH, PA . . .

[0031] A preferred structure for the film according to the present invention comprises the following layers:

[0032] 1. layer A (outer layer) comprising at least 60% s-PP and/or i-PP made by metallocene technology, and from 0 to 40% of at least one resin chosen between SEBS, SEBS with SEB, SEPS, SEPS with SEP and ethylene-1-octene copolymers made by metallocene technology.

[0033] 2. layer B (basic layer) comprising a s-PP/COP blend comprising at least 70% COP, at least 1% s-PP, and from 0 to 25% of at least one resin chosen between SEBS, SEBS with SEB, SEPS, SEPS with SEP and ethylene-1-octene copolymers made by metallocene technology.

[0034] 3. layer C (sealing layer) comprising at least 50% s-PP and/or i-PP made by metallocene technology; from 0 to 40% of at least one resin chosen between SEBS, SEBS with SEB, SEPS, SEPS with SEP and ethylene-1-octene copolymers made by metallocene technology; and at least 1% of a mixture of EVA and EMA.

[0035] and a scraps layer between layers A and B.

[0036] Optionally, this preferred film may comprise an additional layer (B') in between layers B and C, which layer comprises at least 30% by weight of s-PP and/or i-PP made by metallocene technology and from 0 to 70% of at least one resin chosen between SEBS, SEBS with SEB, SEPS, SEPS with SEP and ethylene-1-octene copolymers made by metallocene technology.

[0037] The film according to the present invention is very easy to weld and can therefor very conveniently be used to make bags. Accordingly, the present invention also relates to a bag made of the film described above. Preferably, this bag is a multi-chamber bag including at least one permanent, outer seal and at least one pealable seal. By permanent seal is meant a seal which cannot be pealed easily manually and which generally shows a peel strength of at least 2000 N/m (according to ASTM/ISO F88), or even at least 3000 N/m, while a pealable seal is a seal easy to peal manually and which generally shows a peel strength of less than 2000 N/m. The optimal temperature, pressure and welding time ranges to respectively get a permanent and a pealable seal with a given structure can very easily be determined by one of ordinary skill in the art, using a few experiments. Generally, permanent and pealable seals are made using hot gas or hot tool welding, the latter being preferred.

[0038] The film and bag according to the present invention may be used for any application where their flexibility, sealability, transparency, ability to sterilisation and barrier properties are valuable. The medical field is such an application area. The bag according to the present invention is indeed particularly suitable for containing medical fluids like dialysis, infusion, nutrition . . . solutions. Owe to its excellent barrier properties namely against alcohols and acids, the film according to the present invention can be welded into a bag intended for the storage of acids and alcohols which are for instance used for rinsing or cleaning some medical equipment. One application which gave quite good results is the storage of acetic acid in a double chamber bag, one containing a concentrated solution of acetic acid (up to 50% by weight) and the other, water. Both chambers are separated by a pealable seal, which has to be broken just before use in order to get the acetic acid solution at the right concentration. The bag according to the present invention allows a much longer shelf life than those according to prior art, i.e. less evaporation occurs.

[0039] Finally, the polymer composition according to the present invention can also advantageously be used in injection moulded articles. It is namely so that in most application area of the above mentioned films and bags, the latter have to be connected to some kind of apparatus (like a perfusion or dialysis apparatus for instance) and to perform this connection, often tubes or similar connecting parts are used, which are generally made by injection moulding. In order to have a complete system of the same polymer ingredients, and to benefit of the advantages thereof as set forth above, these injection moulded articles advantageously include the same polymer composition as the one described above.

EXAMPLES

[0040] In the following examples:

[0041] i-PP is grade EOD 9421 from ATOFINA (MFI of 5 according to ASTM D 1238)

[0042] SEBS is grade KRAFO® G 1657 from SHELL

[0043] EVA and EMA are grades U100218 and 16 MA03 from ATOFINA (MFI around 3 and about 18% VA or MA)

[0044] COP is grade TOPAS® 8007 from TICONA (MFI (ISO 1133, 260° C, 2.16 kg) of 30)

[0045] Haze and clarity (=total luminous transmittance) have been measured according to ASTM D 1003-00

[0046] The films were made using a flat die and feed block, by means of co-extrusion, each layer having its own independent single screw extruder (diameter
60 and 45 mm and length of the barrel of 25 D). Temperature settings on die, feed block and adapters were around 220°C. Temperature setting on cylinder from entrance to outlet from 160 to 210/220°C.

[0047] The bags were made by hot tool welding these films under the following conditions: temperature=142°C, pressure=6 bar, time 1,3 seconds.

Comparative Example 1

[0048] A multilayer film with sealable seal characteristics including the following layers was coextruded:

[0049] Layer A (outer layer): blend of i-PP (90 wt %) and SEBS (10 wt %).

[0050] Layer B1: i-PP (100 wt %)

[0051] Layer B2: blend made of i-PP (75 wt %) and SEBS (25 wt %).

[0052] Layer C (sealing layer): blend made of i-PP copolymer (75 wt %), SEBS (22 wt %), EVA (2 wt %) and EMA (1 wt %)

[0053] The total thickness of the film was 200 µm, with a layer B1 of 40 µm. Its haze was 4% and its clarity, 96%.

Comparative Example 2

[0054] Same as comparative example 1 except that layer B1 is made of COP (100 wt %). The total thickness of the film total 200 µm, with a layer B1 of 40 µm. Its haze was 5% and its clarity, 95.5%.

Example 3

A Film According to the Present Invention

[0055] Same as comparative example 1 except that layer B1 is made of a blend of COP (85 wt %) and s-PP (15 wt %).

[0056] The total thickness of the film total 200 µm, with a layer B1 of 40 µm. Its haze was 6.2% and its clarity, 95%.

[0057] Steam-Sterilisation and Drop-Testing:

[0058] 10 bags were made respectively of the films of comparative example 2 and example 3, and were filled with 3 liter water; 5 of each series were steam-sterilised (121°C 250°F, 30 min). After steam-sterilisation, bags made from comparative example 2 showed delamination. The bags according to the present invention (example 3) did not show delamination. Drop-testing of both the sterilised and the not sterilised samples show that bags made according to the present invention survived a drop-test from 2 meter height on a plain floor, while bags made of comparative example 2 did not survive the test.

[0059] Aqueous Acetic Acid Storage:

[0060] Bags made of the film according to comparative example 1 and bags made of the film according to example 3 were filled with 50 ml of aqueous solutions with varying percentages of acetic acid (0, 24, 48, 74, 96%). Total surface area for all bags was 150 cm². The bags were stored at both 25°C and at 40°C for 135 days. Results (average on 2 samples) are given in table 1.

<table>
<thead>
<tr>
<th>% HAc</th>
<th>25°C C.</th>
<th>25°C C.</th>
<th>40°C C.</th>
<th>40°C C.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Comp 1</td>
<td>Example 3</td>
<td>Comp 1</td>
<td>Example 3</td>
</tr>
<tr>
<td>0</td>
<td>0.298</td>
<td>0.244</td>
<td>3.66</td>
<td>2.851</td>
</tr>
<tr>
<td>0.02</td>
<td>0.302</td>
<td>0.317</td>
<td>5.772</td>
<td>3.333</td>
</tr>
<tr>
<td>24</td>
<td>0.26</td>
<td>0.208</td>
<td>3.521</td>
<td>2.49</td>
</tr>
<tr>
<td>48</td>
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<td>0.168</td>
<td>4.136</td>
<td>2.296</td>
</tr>
<tr>
<td>74</td>
<td>0.271</td>
<td>0.098</td>
<td>3.075</td>
<td>1.614</td>
</tr>
<tr>
<td>96</td>
<td>0.402</td>
<td>0.114</td>
<td>9.862</td>
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</tr>
<tr>
<td>96</td>
<td>0.46</td>
<td>0.146</td>
<td>10.327</td>
<td>0.171</td>
</tr>
</tbody>
</table>

with % HAc = the weight percent of acetic acid in the solutions

[0061] As can be seen from the results in table 1 the bags/film/composition made according to the present invention showed significantly lower weight loss. Accordingly, there is less acetic acid leaching out and hence, less smell.

[0062] Mechanical Properties:

[0063] The film according to comparative example 2 shows a strain at break of about 50% and the one according to example 3 shows a strain at break of 150% and a decrease in Elastic modulus (according ASTM D-882/ISO 178/DIN 53457) of 70 Mpa when compared with the film according to comparative example 2. This indicates that the bag/film/ composition made according to the present invention are more flexible than those of prior art.

1. A polymer composition comprising a cyclic olefin polymer (COP) and a syndiotactic polypropylene (s-PP).

2. The polymer composition according to claim 1, wherein said COP is a homo- or copolymer of norbornene with or without side chains.

3. The polymer composition according to claim 1, further comprising at least one resin selected from the group consisting of styrene-ethylene-butylene-styrene (SEBS), SEBS with styrene-ethylene-butylene (SEB), styrene-ethylene-propylene-styrene (SEPS), SEPS with styrene-ethylene-propylene (SEP), and ethylene-1-octene copolymers produced by metallocene technology.

4. A film comprising at least one basic layer comprising said polymer composition according to claim 1.

5. The film according to claim 4, which further comprises at least one side of the basic layer, a layer comprising s-PP and/or isotactic polypropylene (i-PP) produced by metallocene technology and at least one resin selected from the group consisting of styrene-ethylene-butylene-styrene (SEBS), SEBS with styrene-ethylene-butylene (SEB), styrene-ethylene-propylene-styrene (SEPS), SEPS with styrene-ethylene-propylene (SEP), and ethylene-1-octene copolymers produced by metallocene technology.

6. The film according to claim 4, further comprising at least one outer layer comprising s-PP and/or isotactic polypropylene (i-PP) produced by metallocene technology, at least one resin selected from the group consisting of styrene-ethylene-butylene-styrene (SEBS), SEBS with styrene-ethylene-butylene (SEB), styrene-ethylene-propylene-styrene (SEPS), SEPS with styrene-ethylene-propylene (SEP), and ethylene-1-octene copolymers produced by metallocene technology; and
at least one resin selected from the group consisting of ethylene-vinyl-acetate (EVA) and ethylene-methyl acrylate (EMA) copolymers.

7. The film according to claim 4, which comprises:

layer A (outer layer) comprising at least 60% s-PP and/or isotactic polypropylene (i-PP) produced by metallocene technology, and from 0 to 40% of at least one resin selected from the group consisting of styrene-ethylene-butylene-styrene (SEBS), SEBS with styrene-ethylene-butylene (SEB), styrene-ethylene-propylene-styrene (SEPS), SEPS with styrene-ethylene-propylene (SEP), and ethylene-1-octene copolymers produced by metallocene technology;

layer B (basic layer) comprising a s-PP/COP blend comprising at least 70% COP, at least 1% s-PP, and from 0 to 29% of at least one resin selected from the group consisting of styrene-ethylene-butylene-styrene (SEBS), SEBS with styrene-ethylene-butylene (SEB), styrene-ethylene-propylene-styrene (SEPS), SEPS with styrene-ethylene-propylene (SEP), and ethylene-1-octene copolymers produced by metallocene technology;

layer C (sealing layer) comprising at least 50% s-PP and/or isotactic polypropylene (i-PP) produced by metallocene technology; from 0 to 49% of at least one resin selected from the group consisting of styrene-ethylene-butylene-styrene (SEBS), SEBS with styrene-ethylene-butylene (SEB), styrene-ethylene-propylene-styrene (SEPS), SEPS with styrene-ethylene-propylene (SEP), and ethylene-1-octene copolymers produced by metallocene technology; and at least 1% of a mixture of ethylene-vinyl-acetate (EVA) and ethylene-methyl acrylate (EMA) copolymers;

and a scraps layer between said layer A and said layer B.

8. A bag produced by welding said film according to claim 4.

9. The bag according to claim 8 wherein said bag is a multi-chamber bag comprising at least one permanent outer seal and at least one peelable seal.

10. An injection moulded article comprising said polymer composition according to claim 1.