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(54) **Fibre, tapes or filaments comprising a polyethylene composition**

(57) The present invention is directed to fibres, tapes or filaments comprising a polyethylene composition obtainable by polymerization of ethylene using a single site catalyst, to the preparation process thereof, to the use

of said polyethylene composition, as well as articles comprising said fibres, tapes or filaments.

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Description

[0001] This invention relates to fibres, tapes and filaments comprising a polyethylene (PE) composition, to a preparation method thereof, to a use of a polyethylene composition for preparing fibres, tapes or filaments, as well as to articles comprising said fibres, tapes or filaments for wide variety of application areas including technical applications, household applications, as well as interior and sports applications.

Background art

[0002] Polyethylene materials used for fibre, tape and filament products have conventionally been unimodal and produced using Ziegler Natta (znPE) or Chromium catalyst (CrPE). Typically they also have high density, e.g. above 945 kg/m³.

[0003] WO200605370 describes a multimodal polyethylene for drawn tapes, fibres and filaments having a density of at least 940 kg/m³. Such polymers are stated to provide similar or improved properties, such as tenacity, to fibres compared to unimodal polyethylene products in the same density level.

[0004] For example in demanding technical or sports applications such as in sport surfaces, fibres need to withstand heavy mechanical stress and wear. There are also application areas wherein fibres should have good resilience and/tenacity property in order to withstand and/or recover their original state after subjected under a mechanical stress. In certain mechanically demanding application areas, it would sometimes also be beneficial that the fibre material is soft, but at the same time has good mechanical properties. E.g. at least in sport applications, Where fibres are often used as artificial grass material, a soft fibre material would be desirable, optionally together with good UV (ultra violet) light stability. The above properties would be advantageous for fibres in order to maintain a constant performance and/or appearance for longer terms.

[0005] Polypropylene based fibres have been used in prior art for many demanding applications, such as in sport surfaces. However, such prior art fibres may have insufficient softness and UV-stability.

[0006] The abrasion wear resistance of prior art polyethylene, e.g. unimodal polyethylene, fibres is usually not sufficient to maintain a constant performance for longer periods.

[0007] Also in technical application areas i.a. different mechanical property balance is needed for different end use applications.

[0008] It is thus a continuous need for further fibre, tape and filament materials with different property combinations that are suitable or tailored for varying end applications.

The summary of the invention

[0009] It is an object of the present invention to provide an alternative polyethylene composition for fibre, tape and filament production which polyethylene composition provides a fibre product with unexpected combination of properties.

[0010] Another object of the invention is to provide alternative fibres, tapes or filaments comprising a polyethylene composition and exhibiting an excellent property balance useful in various fibre applications, i.a. for technical applications including industrial, agricultural and geological applications, such as ropes, twines, nets, big bags and geo textiles, as well as for household, interior and sports applications, e.g. for synthetic carpet and sport surfaces, such as artificial grass materials for play and sport grounds in indoor or outdoor use.

[0011] Furthermore the invention provides a process for producing fibres, tapes and filaments of the invention, as well as articles comprising said fibres, tapes and filaments.

Brief Description of Drawings

[0012]

Figure 1 shows a graph illustrating the thickness of the samples mLLDPE1, mLLDPE2 and mLLDPE3 of the invention and reference samples PE1, and PE2 before and after a static loading treatment to demonstrate the good resilience property of the Fibre of the invention.

Figure 2 is a graph illustrating the balance between tenacity and elongation at stretch ratios 1:5 and 1:6 measured for the examples mLLDPE1, mLLDPE2 and mLLDPE3 of the invention and reference samples PE1 and PE2.

Description of invention

[0013] Although mPE has differences i.a. in molecular weight distribution and comonomer distribution compared to znPE and CrPE, it has unexpectedly been found that mPE provides an alternative balance between i.a. mechanical

properties useful for fibre, tape or filament applications. Namely, fibres, tapes or filaments comprising an mPE composition have an excellent resilience property and/or tenacity properties which makes said mPE very suitable i.a. for various technical, household, interior and sports applications, wherein one or both of said mechanical properties are desired. Preferably, fibres, tapes or filaments comprising an mPE composition as defined below have advantageous tensile properties expressed as a balance between tenacity and elongation at break. Said resilience property and property balance between tenacity and elongation are further described below and the determination method thereof is defined below under Determination Methods.

[0014] Accordingly the present invention provides a fibre, tape or filament comprising a linear polyethylene composition obtainable by polymerisation of ethylene using a single site catalyst (mPE), wherein said mPE composition has a density of less than 980 kg/m³, preferably less than 975 kg/m³.

[0015] The term "fibre, tapes or filaments" used in this application is shortly abbreviated as "Fibres" and it covers and means all conventional forms known, producible and used in the field of fibres.

[0016] The terms mPE and mLLDPE as defined later below used in this invention mean a linear polyethylene which is produced using a single site catalyst in relative low pressure polymerisation process e.g. in conventional reactor(s) designed for polymerisations using coordination catalysts such as Ziegler Natta, Chromium or single site catalyst. It is thus different from low density polyethylene (LDPE) produced in a high pressure polymerisation in a tubular or an autoclave reactor using typically a free radical initiator. The used terms and the meanings/differences thereof are widely known in the field.

[0017] The present invention covers two equal alternative embodiments (A) and (B).

[0018] In embodiment (A) said Fibre of the invention comprises a mPE composition having a density less than 980 kg/m³, preferably less than 970 kg/m³ as defined above, wherein said mPE is unimodal with respect to molecular weight distribution. Said unimodal mPE present in Fibre can be a homopolymer or copolymer of ethylene. Fibre of embodiment (A) has i.a. excellent tensile properties, more preferably an advantageous balance between tenacity and elongation properties, when measured as defined below under Determination Methods. Fibre (A) has preferably also a very good resilience property. The property balance of Fibre of embodiment (A) makes it very suitable for technical, household, interior and sports applications, particularly for technical applications.

[0019] According to said embodiment (B) of Fibre comprises mPE having a density less than 980 kg/m³, preferably less than 975 kg/m³ as defined above, wherein said mPE is multimodal with respect to molecular weight distribution, and comprises at least (i) a lower weight average molecular weight (LMW) ethylene homopolymer or copolymer component, and (ii) a higher weight average molecular weight (HMW) ethylene homopolymer or copolymer component. Fibre of embodiment (B) has an advantageous resilience property. Preferably, said Fibre of embodiment (B) has preferably also very feasible tensile properties, more preferably a feasible balance between tenacity and elongation properties, when measured as defined below under Determination Methods. The property balance of Fibre of embodiment (B) makes it very suitable for technical, household, interior and sports applications.

[0020] Said Fibre of embodiment (A) and/or (B) may further have i.a. one or more of the following properties: advantageous wear resistance which is also known as abrasion resistance and/or UV stability.

[0021] In one preferable embodiment of Fibre (A) and/or Fibre (B) as defined above, said Fibre of the present invention comprises a linear low density polyethylene composition obtainable by polymerisation of ethylene using a single site catalyst (mLLDPE), wherein said mLLDPE composition has a density of less than 940 kg/m³. The low density of mLLDPE results in softer Fibres which, surprisingly, have at the same time also an excellent resilience property. Accordingly, the resilience property can be maintained together with gained softness property. The property balance thus obtained is very interesting in many application areas including technical and sports applications.

[0022] In one preferable embodiment (a) of said "soft" Fibre, said mLLDPE composition present in Fibre is unimodal with respect to the molecular weight distribution. Fibre of embodiment (a) has preferably the properties given above under embodiment (A) and has additionally very feasible softness making it suitable for various end applications indicated above including technical and sports fibre applications.

[0023] In another preferable embodiment (b) of said "soft" Fibre, said mLLDPE composition present in Fibre is multimodal with respect to molecular weight distribution, and comprises at least (i) a lower weight average molecular weight (LMW) ethylene homopolymer or copolymer component, and (ii) a higher weight average molecular weight (HMW) ethylene homopolymer or copolymer component. Preferably at least one of said LMW and HMW components is a copolymer of ethylene with at least one comonomer. The multimodality of mLLDPE of embodiment (b) contributes also to highly feasible processing properties during the preparation of Fibres. Fibre of embodiment (b) has preferably the properties given above under embodiment (B) and has additionally very feasible softness making it suitable for various end applications indicated above including technical and sports fibre applications, such as sports applications wherein softness is an advantage such as in artificial grass materials.

[0024] As well known to a person skilled in the polymer field, the polyethylene composition having a density of 940 kg/m³ or less may sometimes be defined in the polymer literature as covering i.a. a medium density polyethylene (MDPE) composition and a linear low density ethylene (LLDPE) composition. In this application a polyethylene with a density of

940 kg/m³ or less is abbreviated shortly as "mLLDPE composition" or "mLLDPE" and it naturally covers polyethylenes within the density range of "MDPE". The terms such as "mLLDPE", "metallocene based LLDPE", or "single site based LLDPE" mean that the polyethylene is obtainable by a single site catalyst.

[0025] It is to be understood herein that said mPE present in Fibre of invention may alternatively have a density of more than 940 kg/m³. Fibres comprising mPE having a higher density as defined above or below may also be very useful in various technical end use applications.

[0026] The terms "carpet" and "artificial grass" are also well known expressions and mean that in these products Fibres are attached by any conventional fixing means to a typically flat base or carrier element so that at least one of the fibre ends is freely protruding from the base element. Fibres may also be fixed to the base element from their centre part leaving the Fibre ends with a certain length free and "freely moving". The length of the free "Fibre ends" can vary depending on the desired end application, as well known in the art.

It is also understood that the average diameter/width of Fibre of the invention can vary depending on the end use application.

[0027] Thus the mPE or mLLDPE composition present in said Fibres can be further tailored and optimised in relation to one or more of the additional preferable properties as listed e.g. above, depending on the end use application wherein the Fibre is intended.

The below defined further features, such as further properties or ranges thereof, apply generally to said mPE or mLLDPE present in the Fibre of the invention, to the preparation method of mPE and mLLDPE, to said Fibre of the invention, to the preparation method of Fibre and to articles of the invention comprising said Fibres. And said features can naturally be combined in any combination and in any order to define the preferable subgroups, embodiments and variants of the invention.

mPE Composition

[0028] The term "mLLDPE" is used herein to define mPE compositions having a density of 940 kg/m³ or less. An mPE or mLLDPE composition present in said Fibre as defined above or below may be polymerised by any conventional single site, including metallocene and non-metallocene, catalysis (referred herein as mPE or mLLDPE).

[0029] In one preferable embodiment of Fibre, said mPE or mLLDPE is unimodal with respect to molecular weight distribution. In an alternative preferable embodiment of Fibre said mPE or mLLDPE is multimodal with respect to molecular weight distribution. Unimodal and multimodal mPE or mLLDPE, respectively, both are thus preferable.

By unimodal is meant that the molecular weight profile of the polymer comprises a single peak and is produced by one reactor and one catalyst.

[0030] The term "multimodal" means herein, unless otherwise stated, multimodality with respect to molecular weight distribution and includes also bimodal polymer.

Usually, a polyethylene, e.g. mPE or mLLDPE composition, comprising at least two polyethylene fractions, which have been produced under different polymerization conditions resulting in different (weight average) molecular weights and molecular weight distributions for the fractions, is referred to as "multimodal". The prefix "multi" relates to the number of different polymer fractions present in the polymer.

[0031] Thus, for example, multimodal polymer includes so called "bimodal" polymer consisting of two fractions. The form of the molecular weight distribution curve, i.e. the appearance of the graph of the polymer weight fraction as a function of its molecular weight, of a multimodal polymer will show two or more maxima or is typically distinctly broadened in comparison with the curves for the individual fractions. For example, if a polymer is produced in a sequential multistage process, utilizing reactors coupled in series and using different conditions in each reactor, the polymer fractions produced in the different reactors will each have their own molecular weight distribution and weight average molecular weight. When the molecular weight distribution curve of such a polymer is recorded, the individual curves from these fractions form typically together a broadened molecular weight distribution curve for the total resulting polymer product.

[0032] The multimodal mLLDPE usable in the present invention comprises a lower weight average molecular weight (LMW) component and a higher weight average molecular weight (HMW) component. Said LMW component has a lower molecular weight than the HMW component.

[0033] When present, then one preferable embodiment of said multimodal mPE or mLLDPE comprises at least (i) a lower weight average molecular weight (LMW) ethylene homopolymer or copolymer component, and (ii) a higher weight average molecular weight (HMW) ethylene homopolymer or copolymer component. Preferably, at least one of said LMW and HMW components is a copolymer of ethylene with at least one comonomer. It is preferred that at least said HMW component is an ethylene copolymer. Alternatively, if one of said components is a homopolymer, then said LMW is the preferably the homopolymer.

[0034] Alternatively, when present, said multimodal mPE or mLLDPE may comprise further polymer components, e.g. three Components being a trimodal mPE or mLLDPE. Optionally multimodal mPE or mLLDPE may also comprise e.g. up to 10 % by weight of a well known polyethylene prepolymer which is obtainable from a prepolymerisation step as

well known in the art, e.g. as described in WO9618662. In case of such prepolymer, the prepolymer component is comprised in one of LMW and HMW components, preferably LMW component, as defined above.

[0035] Preferably said multimodal mPE or mLLDPE is bimodal mPE or mLLDPE, respectively, comprising said LMW and HMW components and optionally a prepolymerised fraction as defined above.

[0036] The single site based nature of mPE as defined in claim 1 provides the unexpected effect of the invention, i.e. resilience. In case of preferable mLLDPE also the density provides a further unexpected effect of Fibres, i.e. the balance between softness and mechanical properties. The other properties of said mPE or mLLDPE are not critical and can be varied within the scope of the invention depending on the desired end use application. Accordingly, the below given preferable property ranges are applicable to uni- or multimodal mPE and mLLDPE, unless otherwise stated below. Said mPE composition useful for Fibre has a density of 980 kg/m³ or less, preferably 975 kg/m³ or less, more preferably of 965 kg/m³ or less.

[0037] Said mLLDPE composition useful for Fibre has a density of 940 kg/m³ or less, preferably a density of 938 kg/m³ or less, more preferably a density of 935 kg/m³ or less.

[0038] The lower density limit of said mPE or mLLDPE is typically more than 905 kg/m³, e.g. 910 kg/m³. In another preferable embodiment of "softer" Fibre, even densities of 930 kg/m³ or below, or even 925 kg/m³ or less, are highly feasible.

[0039] Said mPE suitable for Fibre may be a homopolymer or copolymer of ethylene. Said mLLDPE suitable for Fibre is typically a copolymer. The term "ethylene copolymer" or "LLDPE copolymer" as used herein encompasses polymers comprising repeat units deriving from ethylene and at least one other C3-20 alpha olefin monomer. Preferably, mPE or mLLDPE copolymer may be formed from ethylene along with at least one C3-12 alpha-olefin comonomer, e.g. 1-butene, 1-hexene or 1-octene. Preferably, mPE or mLLDPE is a binary copolymer, i.e. the polymer contains ethylene and one comonomer, or a terpolymer, i.e. the polymer contains ethylene and two or three comonomers. Preferably, mPE or mLLDPE comprises an ethylene hexene copolymer, ethylene octene copolymer or ethylene butene copolymer. The amount of comonomer present in mPE or mLLDPE is at least 0.25 mol-%, preferably at least 0.5 mol-%, such as preferably 0.5 to 12 mol%, e.g. 2 to 10 mol-% relative to ethylene. In some embodiments a comonomer range of 4 to 8 mol-% may be desired. Alternatively, comonomer contents present in mPE or mLLDPE may be 1.5 to 10 wt%, especially 2 to 8 wt% relative to ethylene. In any copolymeric HMW component, preferably at least 0.5 mol=%, e.g. at least 1-mol%, such as up to 10 mol-%, of repeat units are derived from said comonomer.

[0040] Said mPE or mLLDPE as defined above or below may have a MFR₂ of 20 g/10 min or less, preferably of 0.1 to 10 g/10min, more preferably of 5 g/10 min or less, when measured according to ISO 1133 at 190°C at load of 2.16 kg. The MFR₂ is typically more than 0.2 g/10 min, preferably 0.5 to 6.0, e.g. 0.7 to 4.0 g/10min.

[0041] Said mPE or mLLDPE suitable for Fibre has preferably a weight average molecular weight (Mw) of 100,000 to 250,000, e.g. 110,000 to 160,000.

[0042] Unimodal mPE or mLLDPE useful for Fibre preferably possesses a narrow molecular weight distribution MWD expressed as Mw/Mn. Said Mw/Mn value of unimodal mPE or mLLDPE is typically less than 30, probably less than 10, more preferably 2 to 4.

[0043] The molecular weight distribution MWD (= Mw/Mn) of a multimodal mPE or mLLDPE suitable for Fibre may be more than 3. The upper limit of Mw/Mn is not critical and may be e.g. less than 40. Mw/Mn is preferably in the range of 3 to 30, more preferably of 3 to 10, and depending on the end application may even be as in the range of 4 to 8.

[0044] Said LMW component of multimodal mPE or mLLDPE suitable for Fibre has preferably a MFR₂ of at least 50 g/10 min, preferably below 500 g/10 min, e.g. up to 400 g/10 min, such as between 100 to 400 g/10 min. The weight average molecular weight (Mw) of the LMW component is preferably in the range of 15,000 to 50,000, e.g. of 20,000 to 40,000.

[0045] The density of LMW component of said multimodal mPE or mLLDPE may range from 930 to 980 kg/m³, e.g. 930 to 970 kg/m³, more preferably 935 to 960 kg/m³ in case of a LMW copolymer component, and 940 to 980 kg/m³, especially 960 to 975 kg/m³ in case of a LMW homopolymer component.

[0046] The LMW component of said multimodal mPE or mLLDPE has preferably from 30 to 70 wt%, e.g. 40 to 60% by weight of the multimodal LLDPE with the HMW component forming 70 to 30 wt%, e.g. 40 to 60% by weight. In one embodiment said HMW component forms 50 wt% or more of the multimodal mPE or mLLDPE as defined above or below.

[0047] The HMW component of said multimodal mPE or mLLDPE has a lower MFR₂ and a lower density than the LMW component.

[0048] The HMW component of said mPE or mLLDPE has preferably an MFR₂ of less than 1 g/10 min, preferably less than 0.5 g/10 min, especially less than 0.2 g/10min. The density of HMW component may be above 900 kg/m³, preferably a density of 910 to 930, e.g. up to 925 kg/m³. The Mw of the higher molecular weight component may range from 100,000 to 1,000,000, preferably 250,000 to 500,000.

Preparation of mPE or mLLDPE polymer

[0049] The mPE or mLLDPE suitable as a Fibre material of the invention can be any conventional, e.g. commercially available, polymer composition. Useful mPE or mLLDPE polymers are available from, without limiting to these, i.a. from Borealis e.g. under trademark Borecene™ FMXXXX, such as Borecene™ FM5220, Borecene™ FM5340 etc.

[0050] Alternatively, suitable mPE or mLLDPE polymer compositions can be produced in a known manner according to or analogously to conventional polymerisation processes, including solution, slurry and gas phase processes, described in the literature of polymer chemistry.

[0051] Unimodal mPE or mLLDPE useful in the present invention is preferably prepared using a single stage polymerisation, e.g. solution, slurry or gas phase polymerisation, preferably a slurry polymerisation in slurry tank or, more preferably, in loop reactor in a manner well known in the art. As an example, said unimodal mPE or mLLDPE can be produced e.g. in a single stage loop polymerisation process according to the principles given below for the polymerisation of low molecular weight fraction in a loop reactor of a multistage process, naturally with the exception that the process conditions (e.g. hydrogen and comonomer feed) are adjusted to provide the properties of the final unimodal polymer.

[0052] Multimodal (e.g. bimodal) mPE or mLLDPE useful in the present invention can be obtainable by mechanical blending two or more, separately prepared polymer components or, preferably, by in-situ blending in a multistage polymerisation process during the preparation process of the polymer components. Both mechanical and in-situ blending are well known in the field.

[0053] Accordingly, preferred multimodal mPE or mLLDPE polymers, when used, are obtainable by in-situ blending in a multistage, i.e. two or more stage, polymerization process including solution, slurry and gas phase process, in any order. Alternatively said multimodal mPE or mLLDPE may be obtainable by using two or more different polymerization catalysts, including multi- or dual site catalysts, in a one stage polymerization.

[0054] Suitable multimodal mPE or mLLDPE is preferably produced in at least two-stage polymerization using the same single site catalyst. Thus, for example two slurry reactors or two gas phase reactors, or any combinations thereof, in any order can be employed. Preferably however, the multimodal mPE or mLLDPE is made using a slurry polymerization in a loop reactor followed by a gas phase polymerization in a gas phase reactor.

[0055] A loop reactor - gas phase reactor system is well known as Borealis technology, i.e. as a BORSTAR® reactor system. Any multimodal mPE or mLLDPE present in the Fibre of the invention is thus preferably formed in a two stage process comprising a first slurry loop polymerisation followed by gas phase polymerisation. Such multistage process is disclosed e.g. in EP517868.

[0056] The conditions used in such a process are well known. For slurry reactors, the reaction temperature will generally be in the range 60 to 110°C, e.g. 85-110°C, the reactor pressure will generally be in the range 5 to 80 bar, e.g. 50-65 bar, and the residence time will generally be in the range 0.3 to 5 hours, e.g. 0.5 to 2 hours. The diluent used will generally be an aliphatic hydrocarbon having a boiling point in the range -70 to +100°C. In such reactors, polymerization may if desired be effected under supercritical conditions. Slurry polymerisation may also be carried out in bulk where the reaction medium is formed from the monomer being polymerised.

[0057] For gas phase reactors, the reaction temperature used will generally be in the range 60 to 115°C, e.g. 70 to 110°C, the reactor pressure will generally be in the range 10 to 25 bar, and the residence time will generally be 1 to 8 hours. The gas used will commonly be a non-reactive gas such as nitrogen or low boiling point hydrocarbons such as propane together with monomer, e.g. ethylene.

[0058] As an example a chain-transfer agent, preferably hydrogen, is added as required to the reactors, and at least 100 to preferably at least 200, and up to 1500, preferably up to 800 moles of H₂/kmoles of ethylene are added to the loop reactor, when the LMW fraction is produced in this reactor, and 0 to 60 or 0 to 50 moles of H₂/kmoles of ethylene, and, again depending on the desired end application, in certain embodiments even up to 100, or up to 500 moles of H₂/kmoles of ethylene are added to the gas phase reactor when this reactor is producing the HMW fraction.

[0059] Preferably, the LMW polymer fraction is produced in a continuously operating loop reactor where ethylene is polymerised in the presence of a polymerization catalyst as stated above and a chain transfer agent such as hydrogen. The diluent is typically an inert aliphatic hydrocarbon, preferably isobutane or propane. The reaction product is then transferred, preferably to continuously operating gas phase reactor. The HMW component can then be formed in a gas phase reactor using preferably the same catalyst.

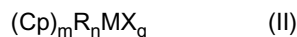
[0060] Prepolymerisation step may precede the actual polymerisation process.

[0061] Where the HMW component is made as a second step in a multistage polymerisation it is not possible to measure its properties directly. However, e.g. for the above described polymerisation process of the present invention, the density, MFR₂ etc of the HMW component can be calculated using Kim McAuley's equations. Thus, both density and MFR₂ can be found using K. K. McAuley and J. F. McGregor: On-line Inference of Polymer Properties in an Industrial Polyethylene Reactor, AIChE Journal, June 1991, Vol. 37, No. 6, pages 825-835. The density is calculated from McAuley's equation 37, where final density and density after the first reactor is known. MFR₂ is calculated from McAuley's equation 25, where final MFR₂ and MFR₂ after the first reactor is calculated.

[0062] The unimodal or multimodal mPE or mLLDPE, as defined above or below, useful in the present invention may be made using any conventional single site catalysts, including metallocenes and non-metallocenes as well known in the field. The choice of an individual catalyst used to make mLLDPE is not critical.

[0063] Preferably said catalyst is one comprising a metal coordinated by one or more η -bonding ligands. Such η -bonded metals are typically transition metals of Group 3 to 10, e.g. Zr, Hf or Ti, especially Zr or Hf. The η -bonding ligand is typically an η^5 -cyclic ligand, i.e. a homo or heterocyclic cyclopentadienyl group optionally with fused or pendant substituents. Such single site, preferably metallocene, procatalysts have been widely described in the scientific and patent literature for about twenty years. Procatalyst refers herein to said transition metal complex.

[0064] The metallocene procatalyst may have a formula II:



wherein:

each Cp independently is an unsubstituted or substituted and/or fused homo- or heterocyclopentadienyl ligand, e.g. substituted or unsubstituted cyclopentadienyl, substituted or unsubstituted indenyl or substituted or unsubstituted fluorenyl ligand;

the optional one or more substituent(s) being independently selected preferably from halogen, hydrocarbyl (e.g. C_1 - C_{20} -alkyl, C_2 - C_{20} -alkenyl, C_2 - C_{20} -alkynyl, C_3 - C_{12} -cycloalkyl, C_6 - C_{20} -aryl or C_7 - C_{20} -arylalkyl), C_3 - C_{12} -cycloalkyl which contains 1, 2, 3 or 4 heteroatom(s) in the ring moiety, C_6 - C_{20} -heteroaryl, C_1 - C_{20} -haloalkyl $-\text{SiR}^n_3$, $-\text{OSiR}^n_3$, $-\text{SR}^n$, $-\text{PR}^n_2$ or $-\text{NR}^n_2$,

each Rⁿ is independently a hydrogen or hydrocarbyl, e.g. C_1 - C_{20} -alkyl, C_2 - C_{20} -alkenyl, C_2 - C_{20} -alkynyl, C_3 - C_{12} -cycloalkyl or C_6 - C_{20} -aryl; or e.g. in case of $-\text{NR}^n_2$, the two substituents Rⁿ can form a ring, e.g. five- or six-membered ring, together with the nitrogen atom to which they are attached;

R is a bridge of 1-7 atoms, e.g. a bridge of 1-4 C-atoms and 0-4 heteroatoms, wherein the heteroatom(s) can be e.g. Si, Ge and/or O atom(s), wherein each of the bridge atoms may bear independently substituents, such as C_1 - C_{20} -alkyl, tri(C_1 - C_{20} -alkyl)silyl, tri(C_1 - C_{20} -alkyl)siloxy or C_6 - C_{20} -aryl substituents; or a bridge of 1-3, e.g. one or two, hetero atoms, such as silicon, germanium and/or oxygen atom(s), e.g. $-\text{SiR}^1_2$, wherein each R¹ is independently C_1 - C_{20} -alkyl, C_6 - C_{20} -aryl or tri(C_1 - C_{20} -alkyl)silyl= residue, such as trimethylsilyl;

M is a transition metal of Group 3 to 10, preferably of Group 4 to 6, such as Group 4, e.g. Ti, Zr or Hf, especially Hf; each X is independently a sigma-ligand, such as H, halogen, C_1 - C_{20} -alkyl, C_1 - C_{20} -alkoxy, C_2 - C_{20} -alkenyl, C_2 - C_{20} -alkynyl, C_3 - C_{12} -cycloalkyl, C_6 - C_{20} -aryl, C_6 - C_{20} -aryloxy, C_7 - C_{20} -arylalkyl, C_7 - C_{20} -arylalkenyl, $-\text{SR}^n$, $-\text{PR}^n_3$, $-\text{SiR}^n_3$, $-\text{OSiR}^n_3$, $-\text{NR}^n_2$ or $-\text{CH}_2\text{-Y}$, wherein Y is C_6 - C_{20} -aryl, C_6 - C_{20} -heteroaryl, C_1 - C_{20} -alkoxy, C_6 - C_{20} -aryloxy, NR^n_2 , $-\text{SR}^n$, $-\text{PR}^n_3$, $-\text{SiR}^n_3$, or $-\text{OSiR}^n_3$;

each of the above mentioned ring moieties alone or as a part of another moiety as the substituent for Cp, X, Rⁿ or R¹ can further be substituted e.g. with C_1 - C_{20} -alkyl which may contain Si and/or O atoms;

n is 0, 1 or 2, e.g. 0 or 1,

m is 1, 2 or 3, e.g. 1 or 2,

q is 1, 2 or 3, e.g. 2 or 3,

wherein m+q is equal to the valency of M.

[0065] Suitably, in each X as $-\text{CH}_2\text{-Y}$, each Y is independently selected from C_6 - C_{20} -aryl, NR^n_2 , $-\text{SiR}^n_3$ or $-\text{OSiR}^n_3$. Most preferably, X as $-\text{CH}_2\text{-Y}$ is benzyl. Each X other than $-\text{CH}_2\text{-Y}$ is independently halogen, C_1 - C_{20} -alkyl, C_1 - C_{20} -alkoxy, C_6 - C_{20} -aryl, C_7 - C_{20} -arylalkenyl or $-\text{NR}^n_2$ as defined above, e.g. $-\text{N}(\text{C}_1\text{-C}_{20}\text{-alkyl})_2$.

[0066] Preferably, q is 2, each X is halogen or $-\text{CH}_2\text{-Y}$, and each Y is independently as defined above

[0067] Cp is preferably cyclopentadienyl, indenyl, tetrahydroindenyl or fluorenyl, optionally substituted as defined above.

[0068] In a suitable subgroup of the compounds of formula II, each Cp independently bears 1, 2, 3 or 4 substituents as defined above, preferably 1, 2 or 3, such as 1 or 2 substituents, which are preferably selected from C_1 - C_{20} -alkyl, C_6 - C_{20} -aryl, C_7 - C_{20} -arylalkyl (wherein the aryl ring alone or as a part of a further moiety may further be substituted as indicated above), $-\text{OSiR}^n_3$, wherein Rⁿ is as indicated above, preferably C_1 - C_{20} -alkyl.

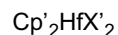
[0069] R, if present, is preferably a methylene, ethylene or a silyl bridge, whereby the silyl can be substituted as defined above, e.g. a (dimethyl)Si=, (methylphenyl)Si= or (trimethylsilylmethyl)Si=; n is 0 or 1; m is 2 and q is two. Preferably, Rⁿ is other than hydrogen.

[0070] A specific subgroup includes the well known metallocenes of Zr, Hf and Ti with two η -5-ligands which may be bridged or unbridged cyclopentadienyl ligands optionally substituted with e.g. siloxy, or alkyl (e.g. C_1 -6-alkyl) as defined above, or with two unbridged or bridged indenyl ligands optionally substituted in any of the ring moieties with e.g. siloxy or alkyl as defined above, e.g. at 2-, 3-, 4- and/or 7-positions. Preferred bridges are ethylene or $-\text{SiMe}_2$.

[0071] The preparation of the metallocenes can be carried out according or analogously to the methods known from the literature and is within skills of a person skilled in the field. Thus for the preparation see e.g. EP-A-129 368, examples of compounds wherein the metal atom bears a $-NR''_2$ ligand see i.a. in WO-A-9856831 and WO-A-0034341. For the preparation see also e.g. in EP-A-260 130, WO-A-9728170, WO-A-9846616, WO-A-9849208, WO-A-9912981, WO-A-9919335, WO-A-9856831, WO-A-00/34341, EP-A-423 101 and EP-A-537 130.

[0072] Alternatively, in a further subgroup of the metallocene compounds, the metal bears a Cp group as defined above and additionally a η^1 or η^2 ligand, wherein said ligands may or may not be bridged to each other. Such compounds are described e.g. in WO-A-9613529, the contents of which are incorporated herein by reference.

[0073] Further preferred metallocenes include those of formula (I)



wherein each X' is halogen, C_{1-6} alkyl, benzyl or hydrogen;

Cp' is a cyclopentadienyl or indenyl group optionally substituted by a C_{1-10} hydrocarbyl group or groups and being optionally bridged, e.g. via an ethylene or dimethylsilyl link. Bis (n-butylcyclopentadienyl) hafnium dichloride and Bis (n-butylcyclopentadienyl) hafnium dibenzyl are particularly preferred.

[0074] Metallocene procatalysts are generally used as part of a catalyst system which also includes a cocatalyst or catalyst activator, for example, an aluminoxane (e.g. methylaluminoxane (MAO), hexaisobutylaluminoxane and tetraisobutylaluminoxane) or a boron compound (e.g. a fluoroboron compound such as triphenylpentafluoroboron or triphenylcarbenium tetraphenylpentafluoroborate $((C_6H_5)_3B+B-(C_6F_5)_4)$). The cocatalysts and activators and the preparation of such catalyst systems is well known in the field.

[0075] If desired the procatalyst, procatalyst/cocatalyst mixture or a proeatalyst/coeatalyst reaction product may be used in unsupported form or it may be precipitated and used as such. One feasible way for producing the catalyst system is based on the emulsion technology, wherein no external support is used, but the solid catalyst is formed from by solidification of catalyst droplets dispersed in a continuous phase. The solidification method and further feasible metallocenes are described e.g. in WO03/051934 which is incorporated herein as a reference.

[0076] Useful activators are, among others, aluminium alkyls and aluminium alkoxy compounds. Especially preferred activators are aluminium alkyls, in particular aluminium trialkyls, such as trimethyl aluminium, triethyl aluminium and triisobutyl aluminium. For instance, when an aluminium alkyl is used as an activator, the molar ratio of the aluminium in the activator to the transition metal in the transition metal complex is from 1 to 500 mol/mol, preferably from 2 to 100 mol/mol and in particular from 5 to 50 mol/mol. Suitable combinations of transition metal complex and activator are disclosed among others, in the examples of WO 95/35323.

[0077] It is also possible to use in combination with the above-mentioned two components different co-activators, modifiers and the like, as is known in the art.

[0078] Any catalytically active catalyst system including the procatalyst, e.g. metallocene complex, is referred herein as single site or metallocene catalyst (system).

[0079] The obtained reaction product of said mLLDPE is typically pelletised in well known manner and the pellets of mLLDPE are then used for Fibre formation.

[0080] The Fibres of the invention may contain other polymer than mLLDPE as well. Preferably the Fibre consists of mLLDPE. The used term "consists of" means herein only that no other polymer components are present in such Fibre embodiment, but naturally said Fibres of such embodiment may comprise conventional fibre additives such as antioxidants, UV stabilisers, colour masterbatches, acid scavengers, nucleating agents, anti-blocking agents, slip agents etc. as well as polymer processing agent (PPA). As well known this can be added to the polymer composition e.g. during the preparation of the polymer or during the fibre preparation process.

Fibre preparation

[0081] The mPE or mLLDPE polymer product as defined above or below, typically in the form of pellets, is converted to Fibres of the invention in a manner well known and documented in the art.

[0082] The fibres can preferably be produced via a film extrusion process, such as cast film or blown film process, via film slitting to produce i.a. tapes, or via a direct extrusion process to produce filaments, preferably monofilaments.

[0083] When Fibres of the invention comprising a mixture of mPE together with other polymer components, then the different polymer components are typically intimately mixed prior to extrusion as is well known in the art.

[0084] According to one commonly used alternative, said mPE or mLLDPE polymer product can be extruded into fibres, tapes or filaments, preferably monofilaments, using known filament extrusion process. One useful process for producing the Fibres of invention is described in "Fiber Technology" Hans A. Krässig, Jürgen Lenz, Herman F. Mark; ISBN: 0-8247-7097-8.

[0085] In a second also commonly used alternative, said mPE or mLLDPE composition may be extruded into a film

which is subsequently cut into fibres and tapes in a known manner. Both preparation methods are conventional and generally known in the production of fibres, tapes and filaments.

[0086] As to the Fibre preparation process wherein a film is first formed and then cut into fibres or tapes: The film may be prepared by any conventional film formation process including extrusion procedures, such as cast film or blown film extrusion, lamination processes or any combination thereof. The film may be mono or multilayer film, e.g. coextruded multilayer film. In case of multilayer film, preferably, the film layers may comprise the same or different polymer composition, whereby at least one layer comprises said mPE or mLLDPE of the invention. Preferably, all layers of a multilayer film comprise, more preferably consist of, the same mPE or mLLDPE composition.

[0087] Particularly preferably the film is formed by blown film extrusion and in case of multilayered film structure by blown film coextrusion processes. Typically said mPE or mLLDPE composition may be blown (co)extruded at a temperature in the range 160°C to 240°C, and cooled by blowing gas (generally air) at a temperature of 10 to 50°C to provide a frost line height of 1 or 2 to 8 times the diameter of the die. The blow up ratio should generally be less than 6, less than 4, more preferably between 1.0 to 1.5, and even more preferably 1.0 to 1.2,

[0088] E.g. the film may be (co)extruded to form first a bubble which is then collapsed and cooled, if necessary, and the obtained tubular film is cut to fibres. Alternatively, the (co)extruded bubble may be collapsed and split into two film laminates. The formed film is then cut to Fibres.

[0089] Alternatively, Fibres can be cut from a cast film that is produced by procedures well known in the field.

[0090] In a very preferable embodiment of the invention Fibres are in stretched, i.e. oriented, form. Preferably Fibres are stretched uniaxially, more preferably in machine direction (MD). Accordingly, in the first direct filament formation alternative, said Fibres can be stretched to a desired draw ratio after extrusion to filaments. In the second Fibre preparation alternative, wherein a film is first formed and cut to Fibres, said film can be stretched before cutting to stretched Fibres, e.g. tapes, or the film is first cut e.g. to tapes and then the formed tapes are stretched to form final Fibres. Preferably the Film is first cut e.g. to tapes which are then stretched to a desired draw ratio to form final Fibres. As to preparation of fibres by first forming a film and cutting it into fibres and tapes, reference can be made to known Lenzing process (for stretching a film prior to cutting into tapes) and Iso process (for cutting a film into tapes and stretching the formed tapes).

[0091] As a preferred embodiment thus stretched Fibres are provided which are preferably in stretched, i.e. oriented, form, preferably in uniaxially oriented form.

[0092] Heat may typically be applied during the stretching, e.g. during in line stretching. The stretching ratio can be determined e.g. by the speed ratio of the godet rolls before and after the heating means in a manner known in the art. As also well known, the stretch and heat setting ratio's can be optimised and adapted depending on the demands of the end application. As heating means e.g. oven or hot plate can be used.

[0093] Accordingly, the Fibre preparation process preferably comprises a step of stretching extruded filaments, of stretching fibres/tapes cut from a film, or of stretching film prior to cutting into fibres/tapes, whereby the stretching is preferably effected in the machine direction (MD) in a draw ratio of at least 1:3.

[0094] A preferable Fibre preparation process thus comprises a step of extruding said mPE or mLLDPE into

- a Fibre which is optionally stretched, preferably in MD, at least 3 times its original length, or
- a film which is optionally stretched, preferably in MD, at least 3 times its original length and subsequently cut to Fibres, or which film is first cut to Fibres that are optionally stretched, preferably in MD, at least 3 times their original length.

[0095] More preferably, extruded fibres, fibres/tapes cut from a film or a film prior to cutting into fibres/tapes is/are stretched 3 to 10 times, its/their original length in the MD. The expressions "stretching 3 times its/their original length" and "drawn down to 3 times its/their original length" mean the same and can also be expressed as a "stretch ratio of at least 1:3" and, respectively, "draw ratio of at least 1:3", wherein "1" represents the original length of the film and "3" denotes that it has been stretched/drawn down to 3 times that original length. Preferred films of the invention are stretched in a draw ratio of at least 1:4, more preferably in the range of 1:5 to 1:8, e.g. in a draw ratio of between 1:5 and 1:7. An effect of stretching, i.e. drawing, is that the thickness of the film is similarly reduced. Thus a draw ratio of at least 1:3 means preferably that also the thickness of the film is at least three times less than the original thickness,

[0096] The Fibres can then be further processed to articles such as ropes, twines, nets, bags or textiles for technical and agricultural use, or i.a. artificial grass for use e.g. in sports grounds etc.

Fibre of the invention

[0097] The Fibre can be in a form of a fibre, tape or filament comprising a unimodal or multimodal mPE or a unimodal or multimodal mLLDPE, preferably a unimodal or multimodal mLLDPE, copolymer as defined above. The Fibre forms part of the invention.

[0098] Preferably, said Fibre consists of a unimodal or multimodal mPE or a unimodal or multimodal mLLDPE copol-

ymers, preferably a unimodal or multimodal mLLDPE copolymer, as defined above or in claims below.

[0099] The term Fibre thus naturally covers fibres, tapes and filaments of any shape and size. The dimensions thereof depend on the end application area, as well known in the art. Filaments are preferably monofilaments.

[0100] In a preferred embodiment Fibre is in stretched form as defined above.

[0101] E.g. when Fibre is produced to a tape form, then such tape, of the invention may typically have a width of at least 0.5 mm, preferably of at least 1 mm. The upper limit of a tape width is not critical and can be e.g. up to 10 mm, preferably up to 6 mm. The thickness of a tape of the invention may be e.g. at least 5 μm , preferably at least 10 μm . Again, the upper limit of a tape thickness is not limited and can be e.g. up to 80 μm , preferably up to 50 μm , in some end applications preferably up to 20 μm . In case of fibres and filaments the dimensions thereof typically correspond to the size range, i.e. dimensions, given above for a tape form. The width ranges and other dimensions given above apply both to Fibres in stretched form and Fibres in non-stretched form. Preferably Fibres are in stretched form and may have the width and other dimensions as defined above.

[0102] As mentioned above, Fibres have an excellent resilience property and/or a very feasible balance between tenacity and elongation. Moreover, Fibres may also be "soft" Fibres comprising mLLDPE as defined above. Further preferably, Fibres may have additionally one or more of the following properties: good UV-stability and/or wear resistance. The application area of Fibres is not limited and it has unexpectedly found that the Fibres and the "soft" Fibres of the invention exhibiting good resilience property are very feasible for many mechanically demanding applications as well. Further preferably, the Fibres show good tensile properties expressed as a balance between tenacity and elongation at break, when measured using tensile tests according to ISO 2062 (year 1993) as defined below under Determination Methods. The samples used for the tensile determinations were prepared as described under Sample Preparation.

[0103] In one embodiment, Fibre of the invention comprises an mPE or mLLDPE as defined above or in claims which mPE or mLLDPE has a tenacity of at least 0.33 N/tex and residual elongation at break of at least 16 %, preferably a tenacity of at least 0.35 N/tex and residual elongation at break of at least 16 %, when measured according to ISO 2062 (year 1993) using a tape sample consisting of said mPE or mLLDPE and drawn to 6 times its original length. In another embodiment, said Fibre comprises a mPE or mLLDPE as defined above or in claims which mPE or mLLDPE has a density of at least 930 kg/m³ and a tenacity of at least 0.33 N/tex and residual elongation at break of at least 30 %, preferably of at least 35 %, when measured according to ISO 2062 (year 1993) using a tape sample consisting of said mPE or mLLDPE and drawn to 6 times its original length. Said method is described below under Determination Methods. The tape sample was prepared as described below under Fibre Sample Preparation.

[0104] Preferably, Fibre of the invention when drawn to 6 times to its original length has a tenacity of at least 0.33 N/tex, preferably 0.35 N/tex, and residual elongation at break of at least 16 %. Alternatively, Fibre of the invention when drawn to 6 times to its original length has a tenacity of at least 0.33 N/tex and residual elongation at break of at least 30 %, preferably a tenacity of at least 0.33 N/tex and residual elongation at break of at least 35 %, when measured according to ISO 2062 (year 1993) as defined below.

[0105] Examples of end application areas are for technical applications including industrial, agricultural and geological applications, household applications, interior applications and sports applications etc.

[0106] The Fibres can be used to prepare articles. The invention thus further provides an article comprising fibres, tapes or filaments as defined above. Examples of articles are i.a. ropes and twines, big bags, nets and geo textiles, as well as synthetic carpet and sport surfaces, such as artificial grass materials for play and sport grounds in indoor or outdoor use, or carpets for private and public premises, such as for corridors, offices and show rooms.

[0107] E.g. in sports surfaces, as artificial grass, the Fibres of the invention can be sufficiently soft and have good wear resistance, i.e. they are resistant to abrasion.

[0108] Preferably they also have good resilience and/or UV stability which is needed especially for outdoor applications.

Determination methods

[0109] Unless otherwise stated, the fibre samples used for the measurements to define the above and below properties of the films were prepared as described under the heading "**Fibre Sample Preparation**". It is naturally to be understood that the properties of Fibre of the invention given above in the description and below in claims are not limited to the Fibre Sample used in the determinations, but apply generally to the Fibre of the invention as defined in claims and/or in preferred embodiments. The Fibre Sample defined herein is merely for meeting the sufficiency/reproducibility of the invention.

[0110] **Density** of the materials is measured according to ISO 1183:1987 (E), method D, with isopropanol-water as gradient liquid. The cooling rate of the plaques when crystallising the samples was 15 C/min. Conditioning time was 16 hours.

[0111] **MFR₂**, **MFR₅** and **MFR₂₁** measured according to ISO 1133 at 190°C at loads of 2.16, 5.0, and 21.6 kg respectively.

[0112] **Molecular weights and molecular weight distribution, Mn, Mw and MWD** were measured by Gel Perme-

ation Chromatography (GPC) according to the following method: The weight average molecular weight M_w and the molecular weight distribution ($MWD = M_w/M_n$ wherein M_n is the number average molecular weight and M_w is the weight average molecular weight) is measured by a method based on ISO 16014-4:2003. A Waters 150CV plus instrument, equipped with refractive index detector and online viscosimeter was used with 3 x HT6E styragel columns from Waters (styrene-divinylbenzene) and 1,2,4-trichlorobenzene (TCB, stabilized with 250 mg/L 2,6-Di tert butyl-4-methyl-phenol) as solvent at 140 °C and at a constant flow rate of 1 mL/min. 500 μ L, of sample solution were injected per analysis. The column set was calibrated using universal calibration (according to ISO 16014-2:2003) with 15 narrow MWD polystyrene (PS) standards in the range of 1.0 kg/mol to 12 000 kg/mol. Mark Houwink constants were used for polystyrene and polyethylene (K: 9.54×10^{-5} dL/g and a: 0.725 for PS, and K: 3.92×10^{-4} dL/g and a: 0.725 for PE). All samples were prepared by dissolving 0.5 - 3.5 mg of polymer in 4 mL (at 140 °C) of stabilized TCB (same as mobile phase) and keeping for 3 hours at 140 °C and for another 1 hours at 160 °C with occasional shaking prior sampling in into the GPC instrument.

[0113] Melting temperature and crystallization temperature, T_m and T_{cr} , both were measured according to ISO 11357-1 on Perkin Elmer DSC-7 differential scanning calorimetry, Heating curves were taken from -10°C to 200°C at 10°C/min. Hold for 10 min at 200°C. Cooling curves were taken from 200°C to -10°C at 10°C per min. Melting and crystallization temperatures were taken as the peaks of endotherms and exotherms. The degree of crystallinity was calculated by comparison with heat of fusion of a perfectly crystalline polyethylene, i.e. 290J/g.

[0114] Comonomer content (mol%) was determined based on Fourier transform infrared spectroscopy (FTIR) determination calibrated with C13-NMR.

[0115] Tenacity and elongation at break were determined by tensile tests. Tensile tests were performed on an Instron apparatus according to the ISO 2062 (year 1993) Norm with the following measuring settings:

Clamping length	250 mm
Drawing speed	250 mm/s
Number of measurements	20
Tensile strength	at break
Elongation	at break

[0116] The tenacity (N/Tex) was calculated from the following equation:

$$(\text{Tensile strength at break})/\text{Tex},$$

wherein Tex = weight (g) of 1000 m fibre

Resilience

[0117] The tapes were tufted onto a plastic carrier. The carrier was a plate with a thickness of 1 cm and contained holes of 1mm through which the tapes could be tufted. The tuft was fixated by clamping a second plate to the bottom of the carrier plate.

Tuft density: 1/10 inch

Pile length: 1 cm

[0118] These samples were subjected to a static loading test. A load of 0.22 N/mm² was applied to the tufted sample during 24 hrs. Thickness of the samples (pool thickness) was measured after removal of the applied pressured at different times and compared with the thickness before the test.

Load: 0,22 N/mm²

Loading time: 24 hrs

Recovery times: 0 min, 15 min, 30 min, 60 min.

Fibre Sample Preparation

[0119] For the above general property definitions and examples wherein determinations using a Fibre sample were used, said Fibre samples were tape samples which were prepared by using a state of the art pilot cast film stretch tape line. The extruder was equipped with a metering pump to ensure a constant output. The water quenching tank, godets and oven used were Riefenhäuser components. The temperature profile of the extruder used was 225 °C, 230°C and

235 °C. The die was kept at 235 °C. Film die had a 0.1 mm gap width. A 75 micron primary film was extruded into a water quench (30°C) water bath. The take of speed of the first godet roll was kept at 10 m/min. Tapes were slit and stretched in a hot air stretching oven with the below indicated stretch ratios, i.e. draw ratios. Annealing was done on the third godet stand. The three rolls of this godets were kept on a temperature of 90, 100 and 100 °C.

Two test sample series with different draw ratios were prepared for each tested PE material: 1. Fibre sample series: tape samples were drawn 5 times their original length (draw ratio of 1:5) and 2. Fibre sample series: tape samples were drawn 6 times their original length (draw ratio of 1:6), unless otherwise stated.

Examples

[0120]

mLLDPE1: A multimodal mLLDPE having a MFR₂ of 1.8 g/10 min and a density of 915 kg/m³.

mLLDPE2 of invention: A unimodal mLLDPE having a MFR₂ of 1.3 g/10 min and a density of 922 kg/m³.

mLLDPE3 of invention: A unimodal mLLDPE polymer had a MFR₂ of 1.3 g/10min and a density of 934 kg/m³.

Reference PE1: A commercially available unimodal CrPE copolymer grade for fibres having a MFR₂ of 0.4 g/10 min and a density of 945 kg/m³.

Reference PE2: A commercially available unimodal znPE copolymer grade for fibres having a MFR₂ of 0.9 g/10 min and a density of 922 kg/m³.

Example 1: Polymerisation of mLLDPE1 of the invention

Catalyst preparation example

[0121] Complex: The catalyst complex used in the polymerisation example was a silica supported bis(n-butyl cyclopentadienyl)hafnium dibenzyl, (n-BuCp)₂Hf(CH₂Ph)₂, and it was prepared according to "Catalyst Preparation Example 2" of WO2005/002744. The starting complex, bis(n-butyl cyclopentadienyl)hafnium dichloride, was prepared as described in "Catalyst Preparation Example 1" of said WO 2005/002744.

Activated catalyst system: Complex solution of 0.80 ml toluene, 38.2 mg (n-BuCp)₂Hf(CH₂Ph)₂ and 2.80 ml 30 wt% methylalumoxane in toluene (MAO, supplied by Albcmarle) was prepared. Precontact time was 60 minutes. The resulting complex solution was added slowly onto 2.0 g activated silica (commercial silica carrier, XPO2485A, having an average particle size 20µm, supplier: Grace). Contact time was 2 h at 24°C. The catalyst was dried under nitrogen purge for 3 h at 50°C. The obtained catalyst had Al/Hf of 200 mol/mol; Hf 0.40 wt%.

Polymerisation example:

[0122] The polymerisation was carried out in a continuously operated pilot polymerisation process. A prepolymerisation step in 50 dm³ loop reactor, at temperature of 60°C and pressure of 63 bar in the presence of the catalyst, ethylene, 1, -butene as a comonomer and propane as diluent in amounts given in table 1 below, preceded the actual polymerisation in two stage loop-gas phase reactor system. The reaction product obtained from prepolymerisation step was fed to the actual loop reactor having a volume 500 dm³ and ethylene, hydrogen, 1-butene as comonomer and propane as diluent were fed in amounts that the ethylene concentration in the liquid phase of the loop reactor was 6,5 mol-%. The other amounts and ratios of the feeds are given in table 1 below. The loop reactor was operated at 85°C temperature and 60 bar pressure. The formed polymer (LMW component) had a melt index MFR₂ of 110 g/10 min at 26 kg/h.

The slurry was intermittently withdrawn from the reactor by using a settling leg and directed to a flash tank operated at a temperature of about 50°C and a pressure of about 3 bar.

From the flash tank the powder, containing a small amount of residual hydrocarbons, was transferred into a gas phase reactor operated at 80°C temperature and 20 bar pressure. Into the gas phase reactor also introduced additional ethylene nitrogen as inert gas as well as 1-butene and 1-hexene as comonomers in such amounts that the ethylene concentration in the circulating gas was 50 mol-%. The ratio of hydrogen to ethylene, the ratio of comonomers to ethylene and the polymer production rate are given in the below table 1. The production rate was 28 kg/h.

The production split between the loop and gas phase reactors was thus 50/50 wt-%.

[0123] The polymer collected from the gas phase reactor was stabilised by adding to the powder 1500ppm Irganox B215. The stabilised polymer was then extruded and pelletised under nitrogen atmosphere with CIM90P extruder, manufactured by Japan Steel Works. The melt temperature was 214 °C, throughput 221 kg/h and the specific energy input (SEI) was 260 kWh/kg. Density and MFR₂ of the final polymer are given in the below table.

Table 1: Polymerisation conditions and the product properties of the obtained products of example 1

Polymerization conditions	Unit	Ex 1 mLLDPE1
Prepolymerisation		
temperature	°C	60
pressure	bar	63
Catalyst feed	g/h	33
C2 feed	kg/h	1,5
C4 feed	g/h	58
H2 feed?		
Loop reactor		
C2 concentration	mol-%	6,5
H2/C2 ratio	mol/kmol	0,56
C4/C2 ratio	mol/kmol	107
C6/C2 ratio	mol/kmol	
MFR ₂	g/10 min.	110
Density	kg/m ³	938
Prod. rate	kg/h	26
Gas phase reactor		
C2 concentration	mol= %	50
H2/C2 ratio	mol/kmol	0,44
C4/C2 ratio	mol/kmol	15
C6/C2 ratio (1-hexene)	mol/kmol	19
Prod. rate	kg/h	28
MFR ₂	g/10 min.	1.9
Density	kg/m ³	914
Final product		
Prod. split loop/GPR	wt%	50/50
Irganox B215	ppm	1500
CIM90P throughput	kg/h	221
CIM90P extruder melt temp.	°C	214
CIM90P SEI (specific energy input)	kWh/kg	260
Pellet properties		
Density of the pelletized final polymer,	kg/m ³	915
MFR ₂ of the pelletized final polymer	g/10 min	1,8

[0124] Example 2: mLLPE2 of invention: A unimodal ethylene hexene copolymer was produced using a bis(n-butylcyclopentadienyl) hafnium dibenzyl catalyst in a slurry loop reactor having a volume 500 dm³ at the polymerization conditions given below. For the preparation of the catalyst system, see example 1 above.

Polymerisation conditions:

[0125]

5	Pressure:	42 bar
	Temperature:	86°C
	C2 amount in flash gas:	5 wt%
	C6/C2 in flash gas:	130 mol/kmol
10	Catalyst feed:	15 g/h
	Residence time:	40 to 60 minutes
	Production rate:	30 kg/h

[0126] After collecting the polymer it was blended with conventional additives (stabiliser and polymer processing aid) and extruded into pellets in a counter rotating twin-screw extruder JSW CIM90P. The obtained unimodal mLLDPE polymer had the density of 922 kg/m³ and MFR₂ of 1.3 g/10min.

[0127] mLLDPE3 of invention: A unimodal ethylene hexene copolymer was produced using a bis(n-butylcyclopentadienyl) hafnium dibenzyl catalyst in a slurry loop reactor having a volume 500 dm³ at the polymerization conditions given below. For the preparation of the catalyst system, see example 1 above.

20	Pressure:	42 bar
	C2 amount in flash gas:	5 wt%
	C6/C2 in flash gas:	67 mol/kmol
25	Temperature:	90°C
	Catalyst feed:	15 g/h
	Residence time:	40 to 60 minutes
	Production rate:	30 kg/h

[0128] After collecting the polymer it was blended with conventional additives (stabiliser and polymer processing aid) and extruded into pellets in a counter rotating twin-screw extruder JSW CIM90P. The resulting unimodal mLLDPE polymer had a MFR₂ of 1.3 g/10min and a density of 934 kg/m³.

Mechanical tests

[0129] Test Fibre samples of the invention comprising the mLLDPE polymer material of the invention and the comparative test fibre samples were produced according to the procedure defined under "Fibre Sample Preparation" and tested for mechanical properties listed in Table 1 below and are further illustrated in figures 1 and 2.

[0130] Resilience test: Resilience was determined as described above under Determination Methods. For all other materials tape samples with a draw ratio of 1:6 was used, except for mLLDPE1 of invention, for which the draw ratio was 1:5.

A load of 0.22 N/mm² was applied to the tufted sample for 24 hrs. Thickness of the samples (pool thickness) was measured after removal of the applied pressured and after 1 and 24 h recuperation times and compared with the thickness before the test. The results are given in figure 1. As can be seen from the results all mLLDPE examples mLLDPE1, mLLDPE2 and mLLDPE have clearly better results than the reference materials.

[0131] Tensile tests: The balance between tenacity and elongation was determined for two series of tape samples, i.e. for sample series stretched 5 times their original length and for sample series stretched 6 times their original length.

[0132] The tenacity tests shows that the balance between tenacity and elongation at break of Fibres of the invention is very good compared commercial fibres, Ref. PE1 and PE2, of prior art having higher density. Figure 2 shows that the tenacity can be increased by increasing the draw ratio, whereby still feasible elongation can be maintained.

[0133] Thus in general, even the "softer" Fibre embodiment of the invention provides a very feasible alternative for commercial fibres conventionally used in sports and technical applications. And when the density of mPE is increased, then Fibres with an excellent tenacity/elongation balance can be obtained.

Table 1. Tenacity and elongation test results

Property	mLLDPE1 of inv.	mLLDPE2 of inv.	mLLDPE3 of inv.	Ref. PE1	Ref. PE2
Density	915	922	934	945	922
comonomer	Butene/ hexene	hexene	hexene	hexene	butene
MFR ₂ , g/10min	1,8	1,3	1,3	0,4	0,9
MFR ₂₁ , g/10min	63	25	25	28	28
T _m , °C	119	119	125	127	122
T _{cr} , °C	104	107	113	116	107
Draw Ratio of 1:5					
Tex	175	181	166	147	165
Tenacity, N/tex	0,276	0,287	0,283	0,29	0,279
Elongation at break, %	28,2	39,51	77,14	48,25	23,44
Draw Ratio of 1:6					
Tex	158	147	140	121	136
Tenacity, N/tex	0,359	0,449	0,337	0,383	0,412
Elongation at break, %	16,44	17,05	48,27	25,3	14,4

Claims

1. A fibre, tape or filament comprising a linear polyethylene composition, **characterised in that** said polyethylene composition comprises:

- a linear low density polyethylene composition obtainable by polymerisation of ethylene using a single site catalyst (mPE), wherein said mPE composition has a density of less than 980 kg/m³, preferably less than 975 kg/m³ and comprises

(A) an mPE composition which is unimodal with respect to molecular weight distribution, and/or
(B) an mPE composition which is multimodal with respect to molecular weight distribution, and comprises at least

(i) a lower weight average molecular weight (LMW) ethylene homopolymer or copolymer component, and

(ii) a higher weight average molecular weight (HMW) ethylene homopolymer or copolymer component

2. A fibre, tape or filament as defined in claim 1, wherein said (A) unimodal mPE or (B) multimodal mPE is a linear low polyethylene composition which is obtainable by polymerisation of ethylene using a single site catalyst (mLLDPE), and wherein said mLLDPE composition has a density of less than 940 kg/m³.
3. The fibre, tape or filament of claim 1 or 2, wherein said mLLDPE composition has a density of 938 kg/m³ or less.
4. The fibre, tape or filament according to any of preceding claim, wherein said mLLDPE composition has a density of 935 kg/m³ or less.
5. The fibre, tape or filament according to any of preceding claim, wherein said mLLDPE composition has a MFR₂ of 10 g/10 min or less, preferably 5 g/10 min or less, when measured according to ISO 1133 at 190°C at load of 2.16 kg.
6. The fibre, tape or filament according to any of preceding claim, wherein said mPE composition is multimodal with respect to molecular weight distribution, comprising at least (i) a lower weight average molecular weight (LMW) ethylene homopolymer or copolymer component, and (ii) a higher weight average molecular weight (HMW) ethylene homopolymer or copolymer component, preferably at least one of said LMW and HMW components is a copolymer

of ethylene with at least one comonomer, wherein said multimodal mPE composition has a molecular weight distribution MWD (Mw/Mn) of less than 40, preferably between 10 to 30.

7. The fibre, tape or filament according to any of preceding claim, wherein said mPE composition is unimodal with respect to the molecular weight distribution and has a MWD (Mw/Mn) of less than 10, preferably between 2 to 4.

8. The fibre, tape or filament according to any of preceding claim which is in stretched form, preferably with a draw ratio of at least 3 times its original length (1:3), more preferably with a draw ratio between 1:5 to 1:8.

9. A process for producing a fibre, tape or filament as defined in any of claims 1-8 comprising

- polymerising ethylene monomers in the presence of comonomers and a single site catalyst system, preferably a metallocene catalyst system, in a single site or multistage process to produce a unimodal or, respectively, multimodal mPE as defined in any of claims 1-8,

- processing the obtained mPE into form of a fibre, tape or filament.

10. The process of claim 9, wherein the step of processing mPE, preferably mLLDPE, into fibre, tape or filament comprises an extrusion step to form said mPE, preferably mLLDPE, into

- a fibre, tape or filament which is optionally stretched at least 3 times its original length, or

- a film which is optionally stretched at least 3 times its original length and subsequently cut to fibres, filaments or tapes, or which film is cut to fibres, filaments or tapes that are optionally stretched at least 3 times their original length.

11. A use of a mPE, preferably mLLDPE, composition as defined in any of preceding claims 1-8 or obtainable by a process of claim 9 or 10 for producing fibres, tapes or filaments.

12. The use as defined in claim 11, wherein said mPE is a multimodal mPE, preferably a multimodal LLDPE, composition as defined in any of claims 1-8 or obtainable by a process of claim 9 or 10.

13. The use of claim 11, wherein said mPE is a unimodal mPE, preferably unimodal mLLDPE composition as defined in any of the preceding claims 1-8 or obtainable by a process of claim 9 or 10.

14. An article comprising fibres, tapes or filaments as defined in any of claims 1-8, or obtainable by a process of claim 9 or 10, preferably for technical or sports applications, such as a rope, twine, big bag, net, geo textile, artificial grass or a carpet.

Fig. 1

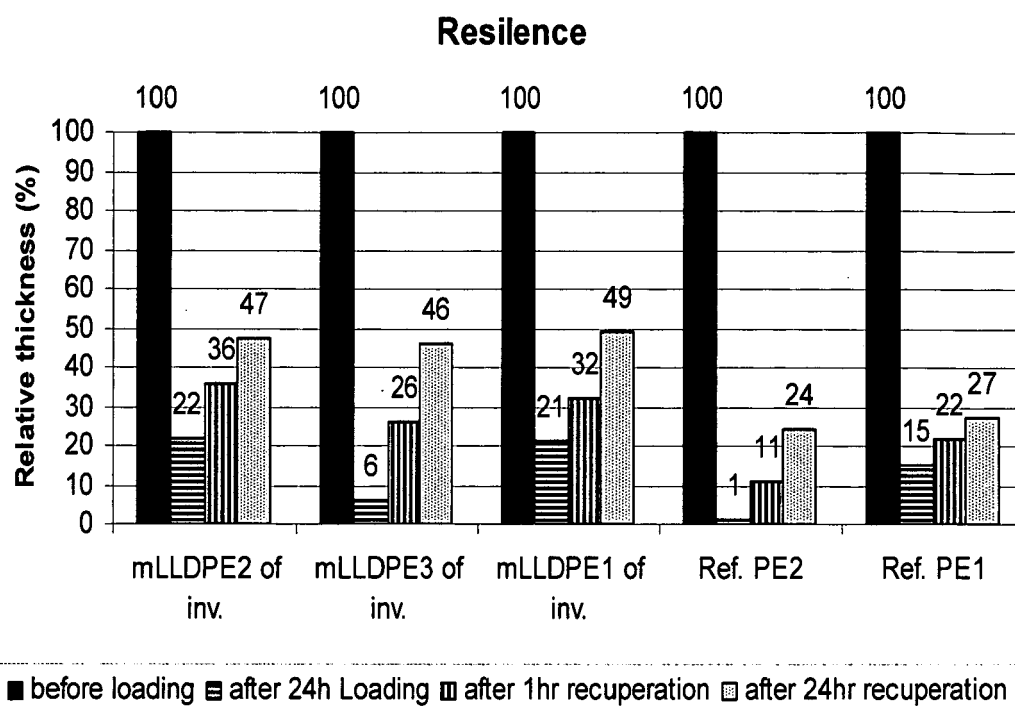
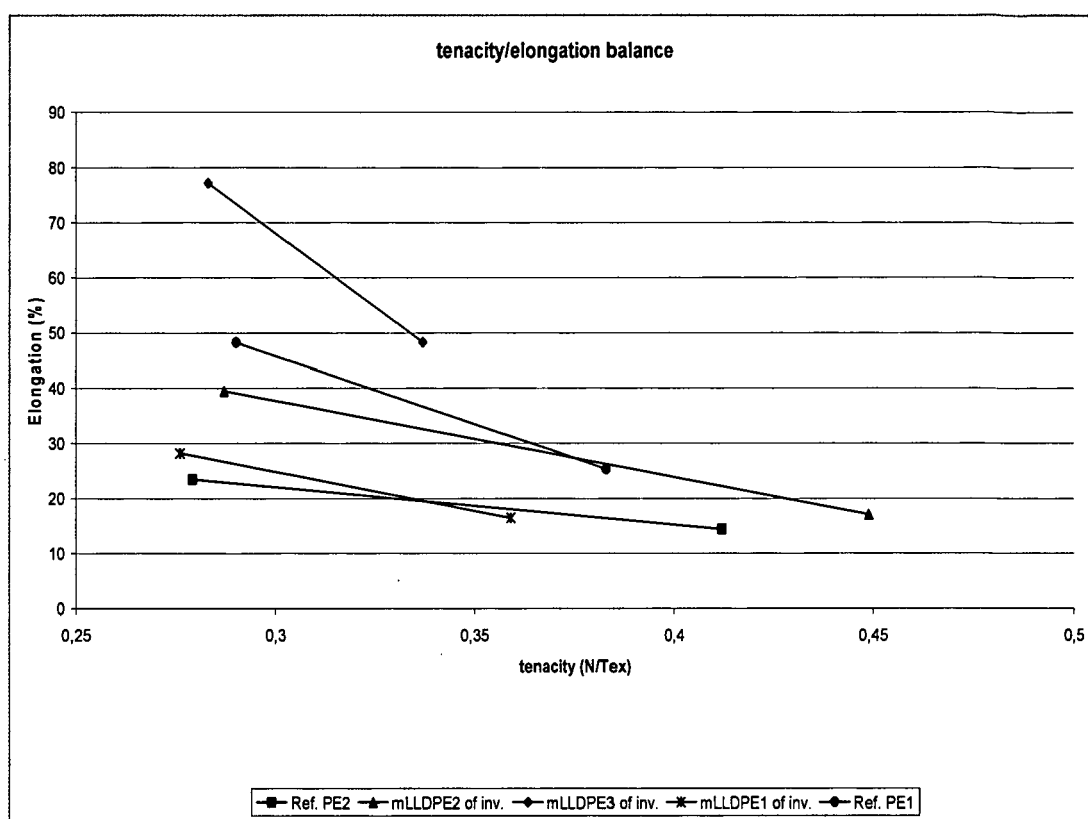


Fig. 2





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EUROPEAN SEARCH REPORT

Application Number
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