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(54) Fibers, tapes or filaments comprising a multimodal polyethylene composition

(57) The present invention is directed to fibres, tapes or filaments comprising a multimodal polyethylene composition, to the preparation process thereof, to the use of a multimodal polyethylene composition, as well as articles comprising said fibres, tapes or filaments.

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Description

[0001] This invention relates to the fibres, tapes and filaments comprising a multimodal polyethylene (PE) composition, to the preparation method thereof, to the use of a multimodal polyethylene composition for preparing fibres, tapes or filaments, as well as articles comprising said fibres, tapes or filaments, 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. Typically they also have high density, e.g. of above 945 kg/m^3.

[0003] WO2006053709 describes a multimodal polyethylene for drawn tapes, fibres and filaments having a density of at least 940 kg/m^3. 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] In very demanding fibre applications, such as in technical or sports applications fibres need to withstand heavy mechanical stress and wear. In some applications, e.g. as sport surface material, it would be beneficial that the fibre material is soft, but at the same time has good abrasion, i.e. wear, resistance. Fibres should also preferably be resilient and/or tenacious in order to recover their original state after subjected under a mechanical stress. Moreover, particularly in outdoor sport fields, where fibres are often used as artificial grass material, a good UV (ultra violet) light stability is needed. The above properties would be advantageous 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 unimodal polyethylene fibres is usually not sufficient to maintain a constant performance, e.g. to guarantee constant sports/playing characteristics of an artificial grass for longer periods.

[0007] 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.

Summary of the invention

[0008] It is an object of the present invention to provide an alternative multimodal polyethylene composition for fibre, tape and filament production which multimodal polyethylene composition provides a fibre product with unexpected combination of properties.

[0009] Another object of the invention is to provide alternative fibres, tapes or filaments comprising a multimodal polyethylene composition and exhibiting an excellent property balance useful for various fibre applications, i.a. for technical applications including industrial, agricultural and geological applications, such as ropes, twines, big bags, nets 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.

[0010] 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

[0011]

Figure 1 shows a scheme of the yarn path in a weaving simulator used in the abrasion resistance test described under Determination Methods.

Figure 2 is a graph illustrating the balance between tenacity and elongation at stretch ratios 1:5 and 1:6 measured for the example znLLDPE1 of the invention and reference examples PE1 and PE2.

Figure 3 is a graph illustrating the abrasion, i.e. wear, resistance of materials of example znLLDPE1 of the invention and reference examples PE1 and PE2 in a weaving simulator, when subjected to a treatment of 6000 cycles under a load (120 g per tape). For each material 5 tape samples were made and the graph shows the number of tapes broken during the test and the number of cycles at the time of fracture.

Description of invention

[0012] The present invention is directed to a fibre, tape or filament comprising a multimodal linear low density polyethylene composition having a density of less than 940 kg/m^3. Due to the low density, softer fibre materials can be provided compared to higher density fibre materials conventionally used in prior art. Surprisingly, the softer fibres, tapes and filaments provided by this invention have an excellent wear resistance expressed also as abrasion resistance. The wear resistance of the fibres, tapes or filaments is at least comparable or may even be improved compared to prior art fibres made from unimodal, higher density polyethylene. Accordingly, the multimodal linear low polyethylene of the present invention is highly suitable alternative material for fibres, tapes or filaments.

[0013] The polyethylene usable in this invention is 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 ZN, Cr 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.

[0014] As well known to a person skilled in the polymer field, the polyethylene composition having a density of 940 kg/m^3 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 multimodal polyethylene with a density of 940 kg/m^3 or less is abbreviated shortly as "multimodal LLDPE composition" or "multimodal LLDPE" and it naturally covers polyethylenes within the density range of "MDPE".

[0015] The term "fibres, 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] In one preferable Fibre embodiment of the invention, said Fibre provides, in addition to above mentioned unexpected balance between softness and wear resistance, preferably also i.a. very feasible tensile properties, expressed as a balance between tenacity and elongation at break properties, when measured as defined below under Determination Methods. Also preferably the Fibres of the invention may further have a good UV stability.

[0017] Thus the multimodal LLDPE material usable in said Fibres can be further tailored and optimised in relation to one or more of the additional preferable properties mentioned in relation to above mentioned Fibre embodiment, depending on the intended end use application.

[0018] Furthermore also the multimodalty of said LLDPE as defined above contributes to the advantageous processing properties in a Fibre preparation process.

[0019] Thus Fibres of the invention are very suitable in wide variety of fibre applications, i.a. for technical applications including industrial, agricultural and geological applications, such as ropes and twines, 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.

[0020] 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 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.

[0021] Also the average diameter/width of Fibre of the invention can vary depending on the end application.

[0022] Thus the multimodal LLDPE 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.

[0023] The below defined further features, such as further properties or ranges thereof, apply generally to said multimodal LLDPE present in the Fibre of the invention, to a preparation method of said multimodal LLDPE, to said Fibre of the invention, to a 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.

Multimodal LLDPE composition

[0024] The multimodal LLDPE composition present in said Fibre as defined above or below may be polymerised using any conventional coordination catalyst. Thus multimodal LLDPE compositions usable in said Fibre include e.g. LLDPE polymerized using a Ziegler Natta catalyst (referred herein as znLLDPE), LLDPE polymerized using a single site catalyst including a metallocene and a non-metallocene catalyst (all single site based LLDPEs are referred herein as mLLDPE) or LLDPE polymerized using a Chromium catalyst. Preferably, multimodal LLDPE composition is a multimodal znLLDPE.

[0025] 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. LLDPE 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. 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, e.g. LLDPE, 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.

[0026] The multimodal LLDPE usable in the present invention comprises preferably 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.

[0027] In one preferred embodiment of Fibre said multimodal LLDPE 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 component is preferably the homopolymer.

[0028] Alternatively, said multimodal LLDPE may comprise further polymer components, e.g. three components being a trimodal LLDPE. Optionally multimodal LLDPE 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.

[0029] Preferably said multimodal LLDPE is bimodal LLDPE comprising said LMW and HMW components and optionally a prepolymerised fraction as defined above.

[0030] The feature of multimodality and density as defined in claim 1 for multimodal LLDPE provides the unexpected effect of the invention, i.a. softness and wear resistance. The other properties of said multimodal LLDPE are not critical and can be varied within the scope of the invention depending on the desired end application use. Accordingly, said multimodal LLDPE composition may have any of the preferred properties given generally below, in any combination.

[0031] Said multimodal LLDPE composition useful in the present invention as defined above or below has preferably a density of 938 kg/m^3 or less. The lower limit is typically more than 905 kg/m^3, preferably 915 kg/m^3 or more, more preferably 920 kg/m^3 or more.

[0032] The melt flow rate, MFR$_2$, of said multimodal LLDPE is preferably in the range of 0.01 to 20 g/10min, e.g. of 0.05 to 10 g/10min, preferably of 0.05 to 6.0 g/10min, more preferably in the range of 0.1 to 5 g/10min. In some Fibre embodiments,

wherein low MFR$_2$ values are desired for LLDPE, then MFR$_2$ of said multimodal LLDPE may be even less than 3 g/10 min, e.g 0.1 to 2.5 g/10min.

[0033] The MFR$_5$ of said multimodal LLDPE as defined above or below may be up to 10 g/10 min, preferably in the range of 0.01 to 5 g/10 min, such as of 0.05 to 4 g/10min. The Mw of LLDPE may be in the range of 100,000 to 300,000, preferably of 150,000 to 270,000. The molecular weight distribution (MWD), Mw/Mn, of a multimodal LLDPE is of at least 5, preferably of at least 8, such as in the range of 10 to 40, preferably of up to 30, and, depending on the end application, also a Mw/Mn in the range of 10 to 25 may be desired.

[0034] 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, said multimodal LLDPE 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, said multimodal LLDPE 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, said multimodal LLDPE comprises an ethylene hexene copolymer, ethylene octene copolymer or ethylene butene copolymer. The amount of comonomer present in said multimodal LLDPE 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 said multimodal LLDPE 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.

[0035] Said LMW component of said multimodal LLDPE as defined above or below may have a MFR$_2$ of at least 50, typically 50 to 3000 g/10 min, preferably at least 100 g/10 min, more preferably 110 to 500 g/10 min. The molecular weight of said LMW component should preferably range from 15,000 to 50,000, e.g. 20,000 to 40,000.
The density of said LMW component may range from 930 to 980 kg/m^3, e.g. 930 to 970 kg/m^3, such as 935 to 960 kg/m^3 in the case of a LMW copolymer, and typically 940 to 980 kg/m^3, preferably 960 to 975 kg/m^3 in case of a LMW homopolymer.

[0036] Said LMW component amounts preferably from 30 to 70 wt%, e.g. 40 to 60% by weight of the total weight of said multimodal LLDPE. Said HMW component forms typically 70 to 30 wt%, e.g. 40 to 60% by weight of said multimodal LLDPE. In one embodiment said HMW component forms 50 wt% or more of the multimodal LLDPE as defined above or below.

[0037] Said HMW component of said multimodal LLDPE as defined above or below has a lower MFR_2 and a lower density than said LMW component. Said HMW component has preferably an MFR_2 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 said HMW component may be above 900 kg/m^3, preferably a density of 910 to 930, e.g. up to 925 kg/m^3. The Mw of HMW component may range from 100,000 to 1,000,000, preferably 250,000 to 500,000.

[0038] In a preferable embodiment of Fibre said multimodal LLDPE as defined above or below is a multimodal znLLDPE copolymer of ethylene with at least one comonomer, as defined above.

Preparation of multimodal LLDPE

[0039] Suitable multimodal LLDPE, preferably znLLDPE, as defined above or below for preparing Fibres of the invention can be any conventional, e.g. commercially available, polymer composition. As an Example of commercially available useful multimodal LLDPE polymers are, without limiting to these, i.a. LLDPE grades available from Borealis e.g. under trademark Borstar® FBXXXX, such as Borstar® FB4370 etc.

[0040] Alternatively, suitable multimodal LLDPE 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.

[0041] Multimodal (e.g. bimodal) LLDPE useful in the present invention can be obtainable by blending two or more, separately prepared polymer components mechanically 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.

[0042] Accordingly, preferred multimodal LLDPE polymers 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 LLDPE may be obtainable by using two or more different polymerization catalysts, including multi- or dual site catalysts, in a one stage polymerization.

[0043] Preferably the multimodal LLDPE is produced in at least two-stage polymerization using the same catalyst, e.g. a single site or Ziegler-Natta 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 LLDPE is made using a slurry polymerization in a loop reactor followed by a gas phase polymerization in a gas phase reactor.

[0044] A loop reactor - gas phase reactor system is well known as Borealis technology, i.e. as a BORSTAR® reactor system. Any multimodal LLDPE 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.

[0045] 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.

[0046] 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.

[0047] 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 H_2/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 H_2/kmoles of ethylene and, again depending on the desired end application, in certain embodiments even up to 100, or up to 500 moles of H_2/ kmoles of ethylene are added to the gas phase reactor when this reactor is producing the HMW fraction.

[0048] Preferably, the lower molecular weight 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.

[0049] Prepolymerisation step may precede the actual polymerisation process.

[0050] 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, MFR_2 etc of the HMW component can be calculated using Kim McAuley's equations. Thus, both density and MFR_2 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. MFR_2 is calculated from McAuley's equation 25, where final MFR_2 and MFR_2 after the first reactor is calculated.

[0051] The multimodal LLDPE, as defined above or below, suitable in the present invention may be made using any conventional catalyst, such as a chromium, single site catalysts, including metallocenes and non-metallocenes as well known in the field, or Ziegler-Natta catalysts as is also known in the art. The preferred are any conventional Ziegler Natta catalysts and the choice of an individual catalyst used to make znLLDPE is not critical.

[0052] In case of a multimodal znLLDPE the polyethylene polymer composition is manufactured using Ziegler-Natta catalysis. Preferred Ziegler-Natta catalysts comprise a transition metal component and an activator. The transition metal component comprises a metal of Group 4 or 5 of the Periodic System (IUPAC) as an active metal. In addition, it may contain other metals or elements, like elements of Groups 2, 13 and 17. Preferably, the transition metal component is a solid. More preferably, it has been supported on a support material, such as inorganic oxide carrier or magnesium halide. Examples of such catalysts are given, among others in WO 95/35323, WO 01/55230, WO 2004/000933, EP 810235 and WO 99/51646.

[0053] In a very preferable embodiment of the invention the polyethylene composition is produced using a Zigler Natta catalysts disclosed in WO 2004/000933 or EP 688794.

[0054] Conventional cocatalysts, supports/carriers, electron donors etc can be used as very well known in the state of art.

[0055] The obtained reaction product of said multimodal LLDPE is typically pelletised in well known manner and the pellets of multimodal LLDPE are then used for Fibre formation.

[0056] The Fibres of the invention may contain other polymer than multimodal LLDPE as well. Preferably the Fibre consists of multimodal LLDPE. Said term "consists of " when used in this application in relation to polymer composition present in Fibre means 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 of during the fibre preparation process.

Fibre preparation

[0057] The multimodal LLDPE 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.

[0058] 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.

[0059] When Fibres of the invention comprising a mixture of multimodal LLDPE together with other polymer components, then the different polymer components are typically intimately mixed prior to extrusion as is well known in the art.

[0060] According to one commonly used alternative, said multimodal LLDPE polymer product can be extruded into fibres, tapes or filaments, preferably monofilaments, using know 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.

[0061] In a second also commonly used alternative, said multimodal LLDPE 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.

[0062] 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 multimodal LLPDE of the invention. Preferably, all layers of a multilayer film comprise, more preferably consist of, the same multimodal LLDPE composition.

[0063] Particularly preferably the film is formed by blown film extrusion and in case of multilayered film structure by blown film coextrusion processes. Typically the LLDPE 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.

[0064] 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.

[0065] Alternatively, Fibres can be cut from a cast film that is produced by procedures well known in the field.

[0066] 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).

[0067] As a preferred embodiment thus stretched Fibres are provided which are preferably in stretched, i.e. oriented, form, preferably in uniaxially oriented form.

[0068] 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.

[0069] 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.
A preferable Fibre preparation process thus comprises a step of extruding the multimodal LLDPE 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.

[0070] 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.

[0071] 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

[0072] The Fibre can be in a form of a fibre, tape or filament comprising a multimodal LLDPE, preferably znLLDPE, copolymer as defined above. The Fibre forms part of the invention.

[0073] Preferably, said Fibre consists of a multimodal LLDPE copolymer, preferably a multimodal znLLDPE copolymer, as defined above or in claims below.

[0074] 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.

[0075] In a preferred embodiment Fibre is in stretched form as defined above.

[0076] 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 no 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.

[0077] As mentioned above, the Fibres have an excellent balance between softness and wear resistance, and preferably one or more of the following properties may also be very advantageous: UV-stability, tenacity and/or resilience

properties. The application area of Fibres is not limited and it has unexpectedly found that the "soft" Fibres of the invention are very feasible for mechanically demanding applications
wherein good mechanical properties, such as good wear resistance, are needed.

[0078] 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.

[0079] In one embodiment Fibre of the invention comprises a multimodal LLDPE as defined above or in claims which multimodal LLDPE has a tenacity of at least 0.40 N/tex and residual elongation at break of at least 13 %, preferably of at least 15 %, when measured according to ISO 2062 (year 1993) using a tape sample consisting of said multimodal LLDPE and drawn to 6 times it original length. Said method is described below under Determination Methods. The tape sample was prepared as described below under Fibre Sample Preparation.

[0080] Preferably, Fibre of the invention when drawn to 6 times to its original length has a tenacity of at least 0.40 N/tex and residual elongation at break of at least 13 %, preferably of at least 15 %, when measured according to ISO 2062 (year 1993) as defined below.

[0081] Examples of end application areas are for technical applications including industrial, agricultural and geological applications, household applications, interior applications and sports applications etc.

[0082] 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.

[0083] E.g. in sports surfaces, as artificial grass, the Fibres of the invention are sufficiently soft and have good wear resistance, i.e. they are resistant to abrasion. Preferably they also have good resilience and/or UV stability which is needed especially for outdoor applications.

Determination methods

[0084] 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.

[0085] **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.

[0086] **MFR_2, MFR_5** and **MFR_{21}** measured according to ISO 1133 at 190°C at loads of 2.16, 5.0, and 21.6 kg respectively.

[0087] **Molecular weights and molecular weight distribution, Mn, Mw and MWD** were measured by Gel Permeation Chromatography (GPC) according to the following method: The weight average molecular weight Mw and the molecular weight distribution (MWD = Mw/Mn wherein Mn is the number average molecular weight and Mw 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 μL 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.

[0088] **Melting temperature and Crystallisation temperature, Tm and Tcr** 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. 290 J/g.

[0089] **Comonomer content (mol%)** was determined based on Fourier transform infrared spectroscopy (FTIR) determination calibrated with C13-NMR.

[0090] **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

[0091] The tenacity (N/Tex) was calculated from the following equation:

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

wherein Tex = weight (g) of 1000 m fibre

Abrasion resistance, i.e. wear resistance, by weaving simulator

[0092] By using a weaving simulator, developed by Centexbel, the abrasion resistance, i.e. wear resistance, was measured on the yarn level. A scheme of the yarn path is given in Fig 1.
During the weaving simulation, the yarns were guided over 3 metallic rods. A bar with the rods was moved up- and downwards during the testing, which causes a friction between the yarns and the metal rods. The abrasion occured over a zone of 2x 10 cm per yarn. Yarn/yarn friction was avoided by using an interspacer bar between the left and right yarn.
Before and after the abrasion treatment, tensile tests were performed on an Instron apparatus according to the ISO 2062 (year 1993) method described above.
The following measuring settings were used:

Weaving simulator:	
Movement frequency:	100/min
Weight:	120 g
Number of cycles:	60000
Number of yarns:	5
Tensile tests:	
Norm:	the ISO 2062 (year 1993)
Clamping length	250 mm
Drawing speed	250 mm/s
Number of measurements	10 (2 tests per abraded test sample: left and right)
Tensile strength	at break
Elongation	at break

Fibre Sample Preparation

[0093] 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 Riefenhhäuser 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

[0094] znLLDPE1 of Invention: A multimodal znLLDPE having a MFR_2 of 0.4 g/10 min, MFR_5 of 2.2 g/10 min and a density of 937 kg/m^3.

[0095] Reference PE1: A commercially available unimodal znPE copolymer grade for fibres having a MFR_2 of 0.60 g/10 min, MFR_{21} of 19 g/10 min and a density of 947 kg/m^3.

[0096] Reference PE2: A commercially available unimodal polyethylene copolymer grade for fibres produced using a Cr catalyst and having a MFR_2 of 0.4 g/10 min, MFR_{21} of 28 g/10 min and a density of 945 kg/m^3.

Examples:

Preparation of Polymers

Example: znLLDPE1 of Invention

[0097] A multimodal znLLDPE1 polymer was prepared in a pilot scale multistage reactor system containing a loop reactor and a gas phase reactor. A prepolymerisation step preceded the actual polymerisation step. The prepolymerisation stage was carried out in slurry in a 50 dm^3 loop reactor at about 80°C in a pressure of about 65 bar using the polymerisation catalyst prepared analogously to Example 3 of EP 688794 using silica support having average particle size of 25 μm and triethylaluminium as the cocatalyst. The molar ratio of aluminium of the cocatalyst to titanium of the catalyst was about 20. Ethylene was fed in a ratio of (200g of C2)/(1g/catalyst). Propane was used as the diluent and hydrogen was feeded in amount to adjust the MFR2 of the prepolymer to about 10 g/10 min.

The obtained slurry together with prepolymerised catalyst and triethyl aluminium cocatalyst were introduced into a 500 dm^3 loop reactor, wherein also a continuous feeds of propane, ethylene and hydrogen were introduced. The feed ratio of H2/C2 was 395 mol/kmol. The loop reactor was operated at 95 °C temperature and 60 bar. The process conditions were adjusted to form polymer having an MFR_2 of 400 g/10 min and a density of about 970 kg/m^3.

[0098] The obtained slurry was then transferred to a fluidised bed gas phase reactor, where also additional ethylene, 1-butene comonomer and hydrogen were added, together with nitrogen as an inert gas to produce the HMW component in the presence of the LMW component. The gas phase reactor was operated at a temperature of 80 °C and a pressure of 20 bar and the feed ratio of H2/C2 and the feed ratio of C4/C2 were adjusted in a manner known to a skilled person to produce prepolymerised final bimodal polymer which, after collecting the polymer, blending with additives and extruding into pellets in a counter rotating twin-screw extruder JSW CIM90P, resulted to a polymer having an MFR_2 of 0.4 g/10 min and density of 937 kg/m^3. The split between the polymer produced in the loop reactor and the polymer produced in the gas phase reactor was 43/57.

Mechanical tests

[0099] Test Fibre samples of the invention comprising the multimodal LLDPE 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 and Table 2 below and are further illustrated in figures 2 and 3.

[0100] 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.

[0101] The tenacity tests shows that the balance between tenacity and elongation at break of Fibre of the invention is very feasible and comparable to present commercial fibres, e.g. Ref. 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.

Thus in general the "softer" Fibres of the invention provide a very feasible alternative for commercial fibres conventionally used in sports and technical applications.

Table 1: Tenacity and elongation test results

Property	znLLDPE 1 of invention	Reference example PE 1	Reference example PE 2
Density, kg/m^3	937	947	945
Comonomer	butene	hexene	hexene
MFR_2, g/10min	0.4	0.60	0.4
MFR_{21}, g/10min	41	19	28

(continued)

Property	**znLLDPE 1 of invention**	**Reference example PE 1**	**Reference example PE 2**
Tm, °C	128	131	127
Draw Ratio of 1:5			
Tex	147	155	147
Tenacity, N/tex	0,313	0,349	0,29
Elongation at break, %	35,9	93,5	48,25
Draw Ratio of 1:6			
Tex	123	129	121
Tenacity, N/tex	0,439	0,417	0,383
Elongation at break, %	15,54	64,74	25,3

[0102] Abrasion Resistance: Wear resistance, i.e. abrasion resistance, was determined as described above under Determination Methods using tape samples which had been stretched 6 times their original length (draw ratio of 1:6). For each material 5 tape samples were subjected to a treatment of 60000 cycles, with a weight load of 120g per tape. After 6000 cycles the test was stopped. For some materials, tapes were broken before the end of the treatment. The mechanical properties were reevaluated after the applied treatment. For each broken tapes, a residual force and elongation of 0% was taken. Figure 3 shows the results of each 5 tape sample of the tested materials and number of cycles at fracture for any broken tapes. Table 2 shows the tensile test results measured from test samples after the "weaving" test. The test shows that Fibres of the invention have very good wear resistance which is improved compared to prior art commercial fibres comprising higher density PE.

Table 2. Residual tensile strength and elongation at break after treatment on the weaving simulator

	Residual strength (%)	Residual elongation (%)
Ref. PE 2	9	10
ZnLLDPE 1 of inv.	37	30
Ref. PE 1	28	69

Claims

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

    - a multimodal linear low density polyethylene (LLDPE) composition which has a density of less than 940 kg/m^3.

2. The fibre, tape or filament of claim 1, wherein said LLDPE composition has a density of 938 kg/m^3 or less.

3. The fibre, tape or filament of claim 1 or 2, wherein LLDPE composition has a MFR$_2$ of 10 g/10 min or less, preferably 5 g/10 min or less, more preferably between 0.1 and 5 g/10 min or less, when measured according to ISO 1133 at 190°C at load of 2.16 kg.

4. The fibre, tape or filament according to any preceding claim, wherein said LLDPE 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, provided that at least one of the LMW and HMW components is a copolymer of ethylene with at least one comonomer.

5. The fibre, tape or filament according to any of preceding claim, wherein said multimodal LLDPE composition has a molecular weight distribution MWD (Mw/Mn) of at least 5, preferably MWD of less than 40, more preferably MWD between 10 to 30.

6. The fibre, tape or filament according to any of preceding claim, wherein said LLDPE composition is obtainable by polymerisation of ethylene and at least one comonomer using a Ziegler Natta catalyst (znLLDPE).

7. The fibre, tape or filament according to any of preceding claim which consists of the multimodal LLDPE as defined in any of the preceding claims, preferably of the multimodal znLLDPE as defined in any of the preceding claims.

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 according to any of preceding claim comprising

- polymerising ethylene monomers in the presence of comonomers and a catalyst system, preferably a Ziegler Natta catalyst system, in a multistage process to produce a multimodal LLDPE as defined in any of claims 1-6, and
- processing said multimodal LLDPE into form of a fibre, tape or filament.

10. The process of claim 9, wherein the processing step of multimodal LLDPE into fiber, tape or filament comprises an extrusion step to form said multimodal LLDPE 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 multimodal LLDPE, preferably a multimodal znLLDPE, composition as defined in any of claims 1-8 or obtainable by a process of claim 9 or 10 for producing fibres, tapes or filaments.

12. 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

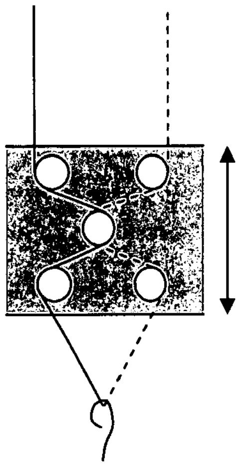


Fig. 2

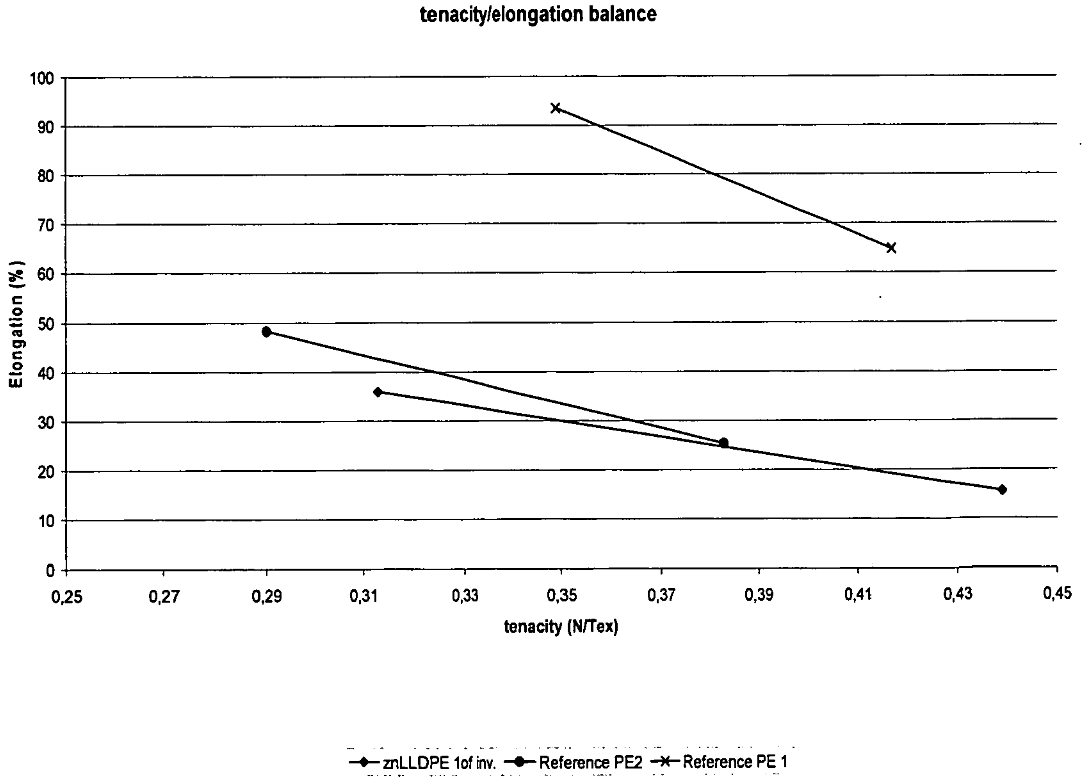
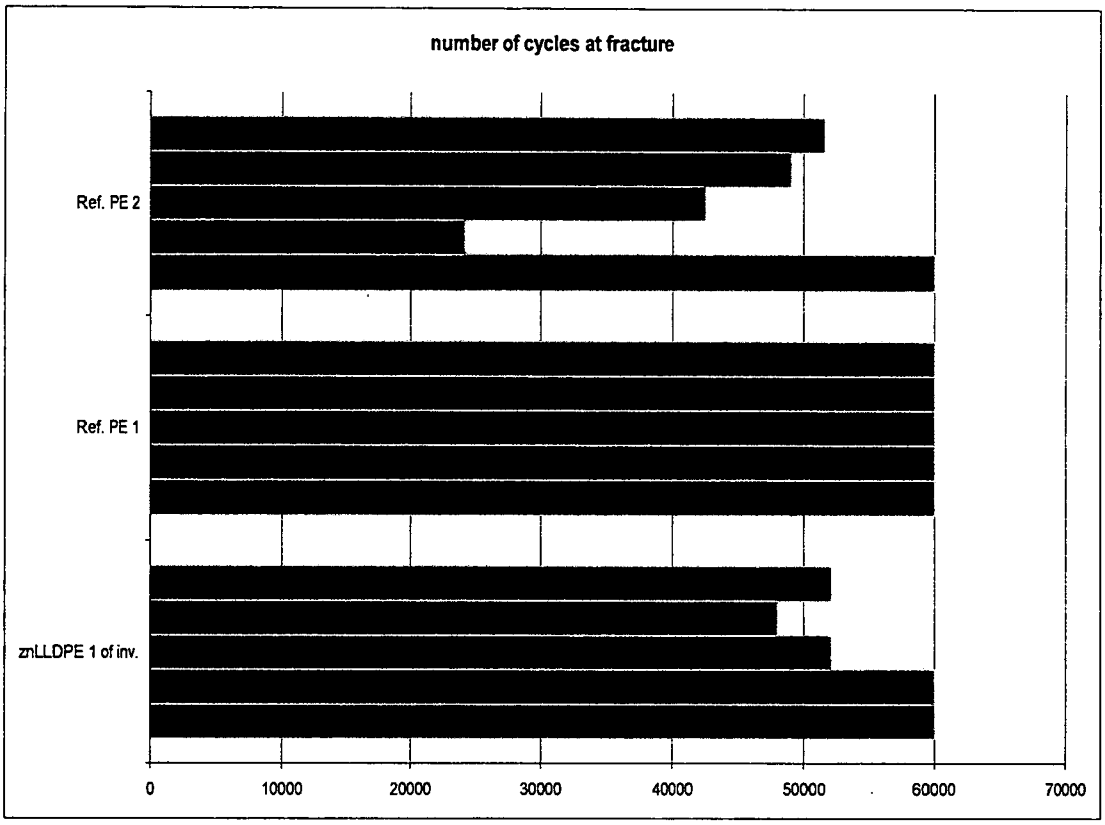

tenacity/elongation balance
Elongation (%)
100
90
80
70
60
50
40
30
20
10
0
0,25
0,27
0,29
0,31
0,33
0,35
0,37
0,39
0,41
0,43
0,45
tenacity (N/Tex)
znLLDPE 1of inv.
Reference PE2
Reference PE 1

Figure 3


number of cycles at fracture
Ref. PE 2
Ref. PE 1
znLLDPE 1 of inv.
0
10000
20000
30000
40000
50000
60000
70000

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 07 00 5908

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	WO 2005/061773 A (COROVIN GMBH [DE]; HABERER MARKUS [DE]; ROETTGER HENNING [DE]) 7 July 2005 (2005-07-07) * page 19, line 33 - page 26, line 36 * -----	1-12	INV. D01F6/04 D01F6/30
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			D01F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	7 August 2007	Lux, Rudolf

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 07 00 5908

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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