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(54) **Title:** PROCESS FOR MANUFACTURING ULTRA-HIGH MOLECULAR WEIGHT POLYETHYLENE CATALYST

(57) **Abstract:** The present invention pertains to a process for manufacturing an ultra-high molecular weight polyethylene, wherein olefin monomers are contacted with a catalytic system under polymerisation conditions under formation of a polyethylene, wherein the catalytic system comprises an active component on a particulate carrier in a site density in the range of $5 \cdot 10^{-9}$ to $5 \cdot 10^{-6}$ mole of catalytic sites per m^2 of carrier surface area, the particulate carrier having an average particle diameter in the range of 1-300 nm, wherein the polyethylene has a weight average molecular weight (Mw) of at least 500 000 gram/mole, and an elastic shear modulus G^0_N , determined directly after melting at 160°C of at most 1.4 MPa.



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Process for manufacturing ultra-high molecular weight polyethylene

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The present invention pertains to process for manufacturing ultra-high molecular weight polyethylene. It also pertains to a method for converting the polyethylene into a polyethylene film.

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EP 1057835 describes a process for the polymerisation of ethylene at a temperature between 250 and 500K with a lanthanide catalyst. It is indicated that the catalyst may in principle be used on a support, but this is not elucidated further. The catalyst is used for the production of polyethylene with a low degree of chain entanglement due to crystallisation of individual chains during polymer formation.

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US 2006/0142521 describes a process for the preparation of a shaped part of an ultrahigh molecular weight polyethylene (UHMWPE) wherein an ultrahigh molecular weight polyethylene with a low degree of entanglement is produced by polymerisation of ethylene at a temperature of 225 to 325K using an unsupported single-site catalyst or a mixture of unsupported single-site catalysts at a catalyst concentration of less than $1 \cdot 10^{-4}$ mol/l.

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WO2009/007045 describes a polyethylene film with high tensile strength that is obtained through the solid state processing of UHMWPE with a Mw/Mn ratio of at most 6 and an elastic shear modulus determined directly after melting at 160°C of at most 0.9 MPa. This document contains only a general description of how the UHMWPE is to be manufactured. It mentions the

possibility of using a catalyst on a support, but does not elucidate anything.

5 There are various disadvantages to the use of unsupported catalysts in the manufacture of polyolefins, in particular of disentangled UHMWPE. In the first place, the use of unsupported catalysts may lead to reactor fouling. Further, most of the industrial processes are based on slurry or gas phase processes, and the nature of the homogeneous catalysts
10 does not make possible to use them in such processes. Moreover, the homogeneous catalysts usually require high quantities of expensive methylaluminoxane (MAO) as a cocatalyst, making the process not of industrial significance.

15 However, it has been found that where it is desired to use a supported catalyst for the manufacture of disentangled UHMWPE, there are specific requirements that should be met to be able to produce a product with good properties. Otherwise, a number of problems may occur. In the first place, there is the
20 significant chance that the polymer product will not be a disentangled material. Further, the polymerization activity drop that is in most cases observed when heterogenizing an homogeneous catalyst, can lead to a system of no significant use.

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Therefore, there is a need for method for polymerisation of ethylene which can be used to manufacture disentangled polyethylene in high activity with high yield. The present invention provides such a process.

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The invention is therefore directed to a process for manufacturing an ultra-high molecular weight polyethylene, wherein olefin monomers are contacted with a catalytic system under polymerisation conditions to form a polyethylene,

wherein the catalytic system comprises an active component on a particulate carrier in a site density in the range of $5 \cdot 10^{-9}$ to $5 \cdot 10^{-6}$ mole of catalytic sites per m^2 of carrier surface area, the particulate carrier having an average
5 particle diameter in the range of 1-300 nm, wherein the polyethylene has a weight average molecular weight (Mw) of at least 500 000 gram/mole, and an elastic shear modulus G_N^0 , determined directly after melting at 160°C of at most 1.4 MPa.

10 It has been found that the selection of the catalyst as specified above allows the manufacture of UHMWPE with a low elastic shear modulus directly after melting, which means that the material has a low degree of entanglement. As will be discussed in more detail below, this material has the
15 advantage that when processed into a film through solid-state processing there is an operating window of about 15°C below the melting point of the polymer. In contrast, when processing conventional, entangled, UHMWPE, the operating window in the stretching step is only about 2°C , which requires extreme
20 process control. Additionally, the use of the UHMWPE of the present invention allows the manufacture of films with high strength and modulus.

Further, analogous to what has been found in other studies, the lifetime of the catalyst is significantly improved by the
25 supportation on a carrier, presumably by hindering bimolecular deactivation processes. For background, reference is made to John R. Severn et al., Chem. Rev., 2005, 105 (11), pp 4073-4147. This leads to longer polymers, with a narrower molecular weight distribution. Last but not least, the supportation
30 considerably reduces the amount of cocatalyst needed.

It is noted that EP989139 describes a catalyst composition for olefin polymerisation, in particular for the manufacture of copolymers having less than 50% crystallinity. This reference

does not describe the manufacture of UHMWPE with the specified elastic shear modulus directly after melting.

The present invention will be discussed in more detail below.

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Figures 1 through 5 show SEM and EDX data of catalysts used in the present invention.

Figure 6 shows a DSC plot of polymer obtained.

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Figure 7 shows rheology data of polyethylene obtained according to the invention.

Figure 8 shows a plot of the polymerization activity (in KgPE/molcat*h*bar) versus the Ti/support

Figure 9 shows a DSC plot of polymer obtained.

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Figure 10 shows MAO supported on hydroxyapatite, and the resulting PE.

Figure 11 shows MAO supported on titania, and the resulting PE.

Figure 12 shows MAO supported on zirconia, and the resulting PE.

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The site density of the catalyst on the carrier is at least $5 \cdot 10^{-9}$ mole of catalytic sites per m^2 of carrier surface area. If the site density is too low, the total number of catalytic sites in the system will be too low, leading to insufficient polymer yield.

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The site density of the catalyst on the carrier is at most $5 \cdot 10^{-6}$ mole of catalytic sites per m^2 of carrier surface area. If the site density is too high, the polymerisation nuclei will be so close together that the polymer molecules will entangle during the polymerisation process, prior to crystallisation. In particular, the site density will be at most $2 \cdot 10^{-6}$ mole/ m^2 , more in particular at most $2 \cdot 10^{-7}$ mole/ m^2

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The site density is the site density of the catalyst, that is, the site density of the polymerisation nucleus. Depending on the type, catalysts may be used with or without an activator.

The site density is calculated as the number of moles of catalyst that are added to the carrier particles, divided by the specific surface area of the carrier particles. This latter value can be determined via BET as is known in the art.

Due to the small particle size of the catalyst particles, the catalyst does not have to be removed from the polymer after polymerisation, but will be further processed with the polymer.

The catalyst particles have an average particle diameter in the range of 1-300 nm. The use of smaller particles is considered preferred, because this will lead to polyethylene with a more disentangled character. Accordingly, it is preferred for the catalyst particle size to be in the range of 1-200 nm, more in particular 1-100 nm, still more in particular 1-50 nm, even more in particular 1-20 nm. The average diameter is determined via dynamic light scattering (DLS), BET, and/or electron microscopy. It is noted that as the presence of active catalyst component will not influence the particle size of the carrier to any measurable extent, the values given in this specification apply equally to the carrier and to the catalyst.

In one embodiment, the relationship between the site density of the catalyst on the carrier and the particle size of the carrier can translate into an average number of sites per carrier particle which is in the range of 1 to 1000.

It is believed that the quality of the polymer will be improved if the number of sites per particle is relatively limited. It is believed that this will reduce the chances of polymer molecules interacting with each other. It is therefore

considered preferred for the average number of sites per carrier particle to be in the range of 1 to 500. The number of sites per catalyst particle will depend, int. al., on the amount of catalyst to be added to the system, and on the particle size of the material. If there are a low number of sites per particle, the number of particles will be relatively high, and this may result in the presence of substantial amounts of carrier material in the system. In one embodiment, the number of sites per particle is in the range of 50-500 sites per particle, e.g., in the range of 100-400 sites per particle more in particular in the range of 150 to 300 sites per particle. In another embodiment, the number of sites per particle is in the range of 1 to 50, still more in particular in the range of 1-10, or even in the range of 1-5. To avoid waste of material, the lower ranges mentioned above are preferably obtained with relatively small particles, e.g., with an average diameter of 1-50 nm, more in particular 1-20 nm, or even smaller.

The average number of sites per carrier particle can be calculated by dividing the number of catalytic sites per gram of the carrier, calculated as indicated below, by the number of carrier particles per gram of the carrier, calculated as indicated below.

The number of catalytic sites per gram carrier can be calculated by dividing the total amount of catalyst molecules added to the carrier particles, by the weight of the carrier particles (in gram).

The number of carrier particles per gram carrier can be calculated from the number average particle and the surface area as follows:

$$\text{number of carrier particles /gram} = \frac{\text{surface area per gram}}{4 * \pi * (1/2 * \text{particle diameter})^2}$$

The average particle size of the particles used in the present invention is defined as the median particle size at the 50th percentile, where 50% of the particles (by number) are greater than the D50 and 50% are smaller than the D50. The particle size distribution may be determined via dynamic light scattering. Depending on the nature of the particles, where the particles are present in a polymer matrix, the polymer matrix can be removed, for example by heating the material to burn off the polymer, followed by determination of the particle size. The particle size can also be determined via scanning electron microscopy or transmission electron microscopy or via other suitable methods known in the art. It is within the scope of the skilled person to select a suitable method.

The carrier particles used in the present invention are generally selected from particles of inorganic oxides, inorganic hydroxides, inorganic carbonates, inorganic alkaline earth metal phosphates, inorganic carbides, inorganic nitrides, carbon nanotubes, clays, and combinations thereof. Within the context of the present specification the indication inorganic oxides also encompasses metal phosphates.

In one embodiment, the carrier particles are selected from oxides of aluminium, silicium, titanium, zirconium, and combinations thereof. In one embodiment, particles of zirconium oxide (zirconia) are used in the present invention. The use of transformation-toughened zirconium oxide may be particularly preferred. Transformation-toughened zirconia, which is commercially available, has a microstructure in which the zirconia is in the tetragonal phase. When transformation toughened zirconia is put under stress, the material will transform from the tetragonal phase into the monoclinic phase. This phase transformation is accompanied by expansion of the

material. Thus, when transformation-toughened zirconia is put under stress, the expansion of the material caused by the phase transformation will stop propagation of cracks formed in the material. Moreover, the presence of zirconia in the polymer matrix will promote delocalisation of stresses generated during impact, thus circumventing the brittle nature of ceramics. Accordingly, transformation-toughened zirconia is capable of absorbing substantial amounts of energy, and its presence in a ballistic material thus helps to dissipate impact energy.

In another embodiment, the carrier particles comprise a carbonate salt of an alkaline earth metal, for example calcium carbonate.

In another embodiment, the carrier particles are particles of an inorganic alkaline earth metal phosphates, such as hydroxyapatite.

In a further embodiment, the carrier particles comprise a nitride or a carbide, in particular a nitride or carbide of silicon or boron.

In one embodiment, the carrier particles are nanotubes, for example carbon nanotubes or boron nitride nanotubes.

In one embodiment, the catalyst system comprises an activator compound and a metallocene or post-metallocene compound wherein at least one of the activator compound and the metallocene compound is present as active component on the particulate carrier. In a preferred embodiment, the activator compound is immobilised on the particulate carrier.

Suitable metallocene or post-metallocene compounds are known in the art. Examples include: bis(cyclopentadienyl)M R₂, bis(indenyl)M R₂, dimethylsilylbis(1-indenyl)M R₂, bis(2,7-di-tert-butylfluorenyl)-ethan-1,2-diyl)M R₂, bis(phenoxy-imine)M R₂, bis(trimethylsilyl) benzamidinateM R₂, pyridyl-amideM R₂,

bridged(bi-aromatic)M R₂, where M can be any transition metal, more in particular Ti, Zr, Hf, and R can be any halogen or alkyl or aryl group, more in particular chloride, methyl or benzyl.

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Activator compounds for olefin polymerisation catalysts are known in the art. Examples of suitable activator compounds include compounds able to alkylate the organometallic complex and ionize it to produce an active olefin polymerization catalyst. Suitable activators are well known in the art. Examples include alumoxanes (methyl alumoxane (MAO), propylmethyl alumoxane (PMAO), ethyl alumoxane, diisobutyl alumoxane), alkylaluminum compounds (triethylaluminum, diethyl aluminum chloride, trimethylaluminum, triisobutyl aluminum), and the like.

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The suitable activator/catalyst combination depends upon the catalyst and the reaction condition used. The use of catalytic systems where MAO can be used as activator compound is considered preferred. The suitable catalyst for the production of UHMWPE should have, in the reaction conditions used, a polymerization rate much higher than the termination rate, where by termination we mean any process that can detach the growing chain from the active metallic centre, so that it terminates the growth of the macromolecular chain.

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The catalyst suitable for use in the present invention may be manufactured by a process which comprises the steps of contacting a particulate carrier sequentially or simultaneously with an activator compound and a metallocene or post-metallocene compound.

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In one embodiment, the particulate carrier is contacted first with the activator compound and then with the metallocene or post-metallocene compound.

In the process according to the invention, an ultra-high molecular weight polyethylene is manufactured by contacting ethylene with a catalytic system as described above under polymerisation conditions under formation of a polyethylene with a weight average molecular weight (Mw) of at least 500 000 gram/mole, and an elastic shear modulus G_N^0 , determined directly after melting at 160°C of at most 1.4 MPa.

10 The conditions that needs to be controlled for polymerization efficiency and to provide polymer of desired properties include: temperature, pressure and the concentrations of various reactants. Polymerisation conditions suitable to yield the UHMWPE with the specified properties will be discussed
15 below.

The polymerisation reaction is carried out at a temperature in the range of 0-100°C, in particular at a temperature in the range of 0-60°C, more in particular at a temperature in the range of below 25°C. At lower temperatures, the polymerisation
20 rate is lower than the crystallisation rate, which ensures that the material crystallises before it can entangle with polymer chains in the vicinity.

As regards pressure, suitable pressures will also vary according to the reactor and polymerization type. The pressure for liquid phase polymerizations is typically less than 69 bar
25 gauge. Pressure for gas phase polymerization is usually in the range of 10-34 bar gauze, more specifically in the range of 10-20 bar gauge, or 14-34 bar gauge.

The ethylene pressure in the process according to the invention generally varies between 1 and 5 bar, more in particular between 1 and 3 bar
30

In one embodiment, the catalyst concentration during the polymerisation is in the range of $1 \cdot 10^{-9}$ mol/l and $5 \cdot 10^{-4}$

mol/l, calculated as mole catalyst on liter of diluent, more in particular, from $1 \cdot 10^{-5}$ mol/l to $1 \cdot 10^{-4}$ mol/l. Depending on the reaction conditions, a too high catalyst concentration will increase the risk of the formation of entanglements. On
5 the other hand, a too low catalyst concentration may lead to a decreased polymer yield.

The reaction can be carried out in the presence of a suitable diluent or solvent. Suitable diluents are liquid under
10 reaction conditions. They serve, int. al., as solvent for the monomer to come in contact with the catalyst. They may also serve as solvent for the cocatalyst. Examples of suitable diluents include, but are not limited to, hydrocarbons such as propane, cyclohexane, isobutane, n-butane, n-pentane,
15 isopentane, neopentane, n-hexane and n-heptane, as well as aromatic solvents as toluene or xylene. Mixtures of solvents may also be used. The solvent should be selected so that it is liquid under reaction conditions. It will be evident to the skilled person which solvents will be liquid under the
20 reaction conditions applied. The use of a mixture of heptane and toluene is considered preferred at this point in time, in particular a mixture containing 25-95% vol.% toluene, in particular 50-95 vol.% toluene, more in particular in the range of 55-80 vol.% toluene. It was found that the use of
25 this particular solvent mixture results in a high polymer yield.

Polymerisation processes are known in the art. The catalysts of the present invention are intended for any olefin
30 polymerization method known in the art, using various types of polymerization reactors. For "polymerization reactor" it is intended any polymerization reactor capable of polymerizing olefin monomers to produce homopolymers or copolymers. The

various types of reactors include batch, slurry, gas-phase, solution, high pressure, tubular or autoclave reactors.

High pressure polymerization reactor may comprise an autoclave reactor. Monomer may be entrained in an inert gaseous stream and introduced at one zone of the reactor. Heat and pressure may be employed appropriately to obtain optimal polymerization reaction conditions. Suitable means are utilized for dissipating the exothermic heat of polymerization.

10 The concentration of various reactants can be controlled to produce resins with certain physical and mechanical properties. The concentrations of monomer, hydrogen, co-catalyst, and electron donors are important in producing these resin properties. Comonomer is used to control product density. Hydrogen is used to control product molecular weight. Co-catalysts can be used to alkylate, scavenge poisons and control molecular weight. The concentration of poisons must be minimized since they will have a deleterious impact on the reactions and product properties. It is within the scope of the common general knowledge of the skilled person to determine the respective parameters.

The polymerisation reaction is generally carried out for a period of 1 minute to 10 hours, depending on polymerisation conditions. If the reaction time is too low, the yield will be insufficient. If the reaction time is too high, little further yield may be obtained, while there is the risk that the polymer chains will entangle. A preferred range for the reaction time may be a period of 30 minutes to 4 hours. It is within the cope of the skilled person to determine the appropriate reaction time.

The present invention also pertains to the polyolefin that can be manufactured using the catalyst system according to the invention.

The polyolefin thus obtained is a polyethylene with a weight
5 average molecular weight (Mw) of at least 500 000 gram/mole
and an elastic shear modulus G_N^0 , determined directly after
melting at 160°C of at most 1.4 MPa, which contains a
particulate catalyst system dispersed therein, the catalytic
10 system comprises an active component on a particulate carrier
in a site density in the range of $5 \cdot 10^{-9}$ to $5 \cdot 10^{-6}$ mole of
catalytic sites per m² of carrier surface area, the
particulate carrier having an average particle diameter in the
range of 1-300 nm.

15 The polyethylene manufactured in the present invention is a
homopolymer of ethylene. Minor amounts of (non-ethylene)
alpha-olefin may be present in the ethylene homopolymer.
Because the presence of other types of monomer will detract
from the properties of the final polymer, the amount of this
20 type of monomer is preferably is at most 10 mole%, more
preferably at most 5 mole%, still more preferably at most 1
mole%, even more preferably at most 0.5 wt.%.

The polyethylene manufactured using the process of the
25 invention is an ultra-high molecular weight polyethylene. An
ultra-high molecular weight polyethylene is a polyethylene
with a weight average molecular weight (Mw) of at least 500
000 gram/mole in particular between $1 \cdot 10^6$ gram/mole and $1 \cdot 10^8$
gram/mole. For determination methods for UHMWPE, reference is
30 made to what is stated in WO2010/007062, page 6, line 25,
through page 8, line 3.

The ultra-high molecular weight polyethylene manufactured
using the catalyst system of the present invention has an

elastic shear modulus G_N^0 determined directly after melting at 160°C of at most 1.4 MPa, in particular 1.0 MPa, more in particular at most 0.9 MPa, still more in particular at most 0.8 MPa, more in particular at most 0.7 MPa. The wording "directly after melting" means that the elastic shear modulus is determined as soon as the polymer has melted, in particular within 15 seconds after the polymer has melted. For this polymer melt G_N^0 typically increases from 0.6 to 2.0 MPa in one, two, or more hours, depending on the molar mass of the polymer.

G_N^0 is the elastic shear modulus in the rubbery plateau region. It is related to the average molecular weight between entanglements M_e , which in turn is inversely proportional to the entanglement density. In a thermodynamically stable melt having a homogeneous distribution of entanglements, M_e can be calculated from G_N^0 via the formula $G_N^0 = g_N \rho RT / M_e$, where g_N is a numerical factor set at 1, ρ is the density in g/cm³, R is the gas constant and T is the absolute temperature in K. A low elastic shear modulus directly after melting stands for long stretches of polymer between entanglements, and thus for a low degree of entanglement. The adopted method for the investigation on changes in G_N^0 with the entanglements formation is the same as described in publications (Rastogi, S., Lippits, D., Peters, G., Graf, R., Yefeng, Y. and Spiess, H., 'Heterogeneity in Polymer Melts from Melting of Polymer Crystals', Nature Materials, 4(8), 1st August 2005, 635-641 and PhD thesis Lippits, D.R., "Controlling the melting kinetics of polymers; a route to a new melt state", Eindhoven University of Technology, dated 6th March 2007, ISBN 978-90-386-0895-2).

It was found that the combination of the low elastic shear modulus directly after melting with the high molecular weight makes for a polymer which can be processed through solid state

processing to yield a high strength high-modulus film with a relatively large operating window.

In one embodiment, the ultra-high molecular weight polyethylene manufactured via the process of the present invention has a relatively narrow molecular weight distribution. This is expressed by the Mw (weight average molecular weight) over Mn (number average molecular weight) ratio of at most 8. More in particular the Mw/Mn ratio is at most 6, still more in particular at most 4, even more in particular at most 2.

The UHMWPE manufactured via the process according to the invention has a DSC crystallinity of at least 74%, more in particular at least 80%. In one embodiment, the UHMWPE has a DSC crystallinity of at least 85%, more in particular at least 90%. DSC crystallinity may be determined as described in WO2010/007062, paragraph bridging pages 13 and 14.

In one embodiment, the disentangled UHMWPE manufactured in accordance with the present invention has a bulk density which is significantly lower than the bulk density of conventional UHMWPEs. More in particular, the UHMWPE manufactured using the catalyst system of the present invention may have a packing density below 0.25 g/cm^3 , in particular below 0.18 g/cm^3 , still more in particular below 0.13 g/cm^3 . The packing density may be determined in accordance with ASTM-D1895. A fair approximation of this value can be obtained as follows. A sample of UHMWPE powder as synthesised is poured into a measuring beaker of exact 100 ml. After scraping away the surplus of material, the weight of the content of the beaker is determined and the packing density is calculated.

Surprisingly it has been found that the presence of catalyst carrier particles hardly interferes with the processing of the ultra-high molecular weight polyethylene. Accordingly, the polyethylene containing refractory particles may be processed to form shaped products according to manners conventional in the art.

In one embodiment, the ultra-high molecular weight polyethylene manufactured using the catalyst system according to the invention is converted to films using a solid state film manufacturing process comprising the steps of subjecting the starting ultra-high molecular weight polyethylene to a compacting step and a stretching step under such conditions that at no point during the processing of the polymer its temperature is raised to a value above its melting point. The compacting step is carried out to integrate the polymer particles into a single object, e.g., in the form of a mother sheet. The stretching step is carried out to provide orientation to the polymer and manufacture the final product. The two steps are carried out at a direction perpendicular to each other. It is noted that it is within the scope of the present invention to combine these elements in a single step, or to carry out the process in different steps, each step performing one or more of the compacting and stretching elements. For example, in one embodiment of the process according to the invention, the process comprises the steps of compacting the polymer powder to form a mothersheet, rolling the plate to form rolled mothersheet and subjecting the rolled mothersheet to a stretching step to form a polymer film. The compacting force applied in the process according to the invention generally is 10-10000 N/cm², in particular 50-5000 N/cm², more in particular 100-2000 N/cm². The density of the material after compacting is generally between 0.8 and 1 kg/dm³, in particular between 0.9 and 1 kg/dm³.

In one embodiment, the compacting and rolling step is carried out at a temperature of at least 1°C below the unconstrained melting point of the polymer, in particular at least 3°C below the unconstrained melting point of the polymer, still more in particular at least 5°C below the unconstrained melting point of the polymer. Generally, the compacting step is carried out at a temperature of at most 40°C below the unconstrained melting point of the polymer, in particular at most 30°C below the unconstrained melting point of the polymer, more in particular at most 10°C. In the process of this embodiment the stretching step is generally carried out at a temperature of at least 1°C below the melting point of the polymer under process conditions, in particular at least 3°C below the melting point of the polymer under process conditions, still more in particular at least 5°C below the melting point of the polymer under process conditions. It is noted that it is due to the low value of the elastic shear modulus directly after melting that processing at a value relatively well below the melting temperature of the polymer can be applied.

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As the skilled person is aware, the melting point of polymers may depend upon the constraint under which they are put. This means that the melting temperature under process conditions may vary from case to case. It can easily be determined as the temperature at which the stress tension in the process drops sharply. Generally, the stretching step is carried out at a temperature of at most 30°C below the melting point of the polymer under process conditions, in particular at most 20°C below the melting point of the polymer under process conditions, more in particular at most 15°C.

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The unconstrained melting temperature of the starting polymer is between 138 and 142°C and can easily be determined by the person skilled in the art. With the values indicated above

this allows calculation of the appropriate operating temperature. The unconstrained melting point may be determined via DSC (differential scanning calorimetry) in nitrogen, over a temperature range of +30 to +180°C. and with an increasing
5 temperature rate of 10°C/minute. The maximum of the largest endothermic peak at from 80 to 170°C is evaluated here as the melting point.

The stretching step in the process according to the invention
10 is carried out to manufacture the polymer film. The stretching step may be carried out in one or more steps in a manner conventional in the art. A suitable manner includes leading the film in one or more steps over a set of rolls both rolling in process direction wherein the second roll rolls faster than
15 the first roll. Stretching can take place, e.g., over a hot plate or in an air circulation oven.

In one embodiment of the present invention the stretching step encompasses at least two individual stretching steps, wherein the first stretching step is carried out at a lower
20 temperature than the second, and optionally further, stretching steps. In one embodiment, the stretching step encompasses at least two individual stretching steps wherein each further stretching step is carried out at a temperature which is higher than the temperature of the preceding
25 stretching step. As will be evident to the skilled person, this method can be carried out in such a manner that individual steps may be identified, e.g., in the form of the films being fed over individual hot plates of a specified temperature. The method can also be carried out in a
30 continuous manner, wherein the film is subjected to a lower temperature in the beginning of the stretching process and to a higher temperature at the end of the stretching process, with a temperature gradient being applied in between. This embodiment can for example be carried out by leading the film

over a hot plate which is equipped with temperature zones, wherein the zone at the end of the hot plate nearest to the compaction apparatus has a lower temperature than the zone at the end of the hot plate furthest from the compaction apparatus. In one embodiment, the difference between the lowest temperature applied during the stretching step and the highest temperature applied during the stretching step is at least 3°C, in particular at least 7°C, more in particular at least 10°C. In general, the difference between the lowest temperature applied during the stretching step and the highest temperature applied during the stretching step is at most 30°C, in particular at most 25°C.

Depending on the properties of the polymer, the total stretching ratio of the film can be relatively high. For example, the total stretching ratio may be at least 80, in particular at least 100, more in particular at least 120, in particular at least 140, more in particular at least 160. The total stretching ratio is defined as the area of the cross-section of the compacted mothersheet divided by the cross-section of the drawn film produced from this mothersheet.

It has also been found that using a polymer manufactured in accordance with the present invention as compared to conventional processing of UHMWPE, materials with a strength of at least 2 GPa can be manufactured at higher deformation speeds. The deformation speed is directly related to the production capacity of the equipment. For economical reasons it is important to produce at a deformation rate which is as high as possible without detrimentally affecting the mechanical properties of the film. In particular, it has been found that it is possible to manufacture a material with a strength of at least 2 GPa by a process wherein the stretching step that is required to increase the strength of the product from 1.5 GPa to at least 2 GPa is carried out at a rate of at least 4% per second. In conventional polyethylene processing

it is not possible to carry out this stretching step at this rate. While in conventional UHMWPE processing the initial stretching steps, to a strength of, say, 1 or 1.5 GPa may be carried out at a rate of above 4% per second, the final steps, required to increase the strength of the film to a value of 2 GPa or higher, must be carried out at a rate well below 4% per second, as otherwise the film will break. In contrast, in the process according to the invention it has been found that it is possible to stretch intermediate film with a strength of 1.5 GPa at a rate of at least 4% per second, to obtain a material with a strength of at least 2 GPa. For further preferred values of the strength reference is made to what has been stated above. It has been found that the rate applied in this step may be at least 5% per second, at least 7% per second, at least 10% per second, or even at least 15% per second.

The strength of the film is related to the stretching ratio applied. Therefore, this effect can also be expressed as follows. In one embodiment of the invention, the stretching step of the process according to the invention can be carried out in such a manner that the stretching step from a stretching ratio of 80 to a stretching ratio of at least 100, in particular at least 120, more in particular at least 140, still more in particular of at least 160 is carried out at the stretching rate indicated above.

In still a further embodiment, the stretching step of the process according to the invention can be carried out in such a manner that the stretching step from a material with a modulus of 60 GPa to a material with a modulus of at least at least 80 GPa, in particular at least 100 GPa, more in particular at least 120 GPa, at least 140 GPa, or at least 150 GPa is carried out at the rate indicated above.

In will be evident to the skilled person that the intermediate products with a strength of 1.5 GPa, a stretching ratio of 80,

and/or a modulus of 60 GPa are used, respectively, as starting point for the calculation of when the high-rate stretching step starts. This does not mean that a separately identifiable stretching step is carried out where the starting material has the specified value for strength, stretching ratio, or modulus. A product with these properties may be formed as intermediate product during a stretching step. The stretching ratio will then be calculated back to a product with the specified starting properties. It is noted that the high stretching rate described above is dependent upon the requirement that all stretching steps, including the high-rate stretching step or steps are carried out at a temperature below the melting point of the polymer under process conditions.

The present invention also pertains to shaped objects comprising the polyethylene comprising refractory particles according to the invention. Shaped objects are, for example, films, tapes, fibres, filaments, and products which contain these materials, such as ropes, cables, nets, fabrics, and protective appliances such as ballistic resistant moulded articles.

Polyethylene films which may be manufactured using the process described above may have a tensile strength of at least 1.0 GPa, a tensile modulus of at least 40 GPa, and a tensile energy-to-break of at least 15 J/g and which comprise 0.001 to 10 weight % of catalyst particles, wherein the refractory particles have an average particle size in the range of 1-300 nm.

In one embodiment, the tensile strength is at least 1.2 GPa, more in particular at least 1.5 GPa, still more in particular at least 1.8 GPa, even more in particular at least 2.0 GPa, still more in particular at least 2.5 GPa, more in particular at least 3.0 GPa, still more in particular at least 4 GPa.

Tensile strength is determined in accordance with ASTM D882-00.

In another embodiment, the tensile modulus is at least 50 GPa. The modulus is determined in accordance with ASTM D822-00.

5 More in particular, the tensile modulus is at least 80 GPa, more in particular at least 100 GPa, still more in particular at least 120 GPa, even more in particular at least 140 GPa, or at least 150 GPa.

In another embodiment, the tensile energy to break is at least
10 20 J/g, in particular at least 25 J/g, more in particular at least 30 J/g, even more in particular at least 35 J/g, still more in particular at least 40 J/g, or at least 50 J/g. The tensile energy to break is determined in accordance with ASTM D882-00 using a strain rate of 50%/min. It is calculated by
15 integrating the energy per unit mass under the stress-strain curve.

In one embodiment of the present invention, the films have a 200/110 uniplanar orientation parameter Φ of at least 3. The 200/110 uniplanar orientation parameter Φ is defined as the
20 ratio between the 200 and the 110 peak areas in the X-ray diffraction (XRD) pattern of the tape sample as determined in reflection geometry. The 200/110 uniplanar orientation parameter gives information about the extent of orientation of the 200 and 110 crystal planes with respect to the tape
25 surface. For a tape sample with a high 200/110 uniplanar orientation the 200 crystal planes are highly oriented parallel to the tape surface. It has been found that a high uniplanar orientation is generally accompanied by a high tensile strength and high tensile energy to break. It may be
30 preferred for the 200/110 uniplanar orientation parameter Φ to be at least 4, more in particular at least 5, or at least 7. Higher values, such as values of at least 10 or even at least 15 may be particularly preferred. The theoretical maximum value for this parameter is infinite if the peak area 110

equals zero. High values for the 200/110 uniplanar orientation parameter are often accompanied by high values for the strength and the energy to break. The 200/110 uniplanar orientation parameter Φ may be determined as is described in
5 WO2010/007062, page 9, line 19, through page 11, line 17.

The shaped object according to the invention may also be a fibre. For the fibres the same preferred ranges apply as have been specified above for the films.

10 Suitable fibres can be obtained from the films as described above, e.g., via slitting. The process as described above will yield tapes. They can be converted into fibres via methods known in the art, e.g., via slitting. They can also be
15 obtained via a process comprising subjecting a polyethylene tape with a weight average molecular weight of at least 100 000 gram/mole, an Mw/Mn ratio of at most 6, and a 200/110 uniplanar orientation parameter of at least 3 to a force in the direction of the thickness of the tape over the whole width of the tape. Again, for further elucidation and
20 preferred embodiments as regards the molecular weight and the Mw/Mn ratio of the starting tape, reference is made to what has been stated above.

In one embodiment of the present invention, the fibres have a 020 uniplanar orientation parameter of at most 55°. The 020
25 uniplanar orientation parameter gives information about the extent of orientation of the 020 crystal planes with respect to the fiber surface. The 020 uniplanar orientation parameter preferably is at most 45°, more preferably at most 30°. In some embodiments the 020 uniplanar orientation value may be at
30 most 25°. It has been found that fibres which have a 020 uniplanar orientation parameter within the stipulated range have a high strength and a high elongation at break. For further information and a determination method of this

parameter, reference is made to page 11, line 19 through page 13, line 17, of WO2010/007062.

In one embodiment, the width of the film is generally at least 5 mm, in particular at least 10 mm, more in particular at least 20 mm, still more in particular at least 40 mm. The width of the film is generally at most 200 mm. The thickness of the film is generally at least 8 microns, in particular at least 10 microns. The thickness of the film is generally at most 150 microns, more in particular at most 100 microns. In one embodiment, films are obtained with a high strength, as described above, in combination with a high linear density. In the present application the linear density is expressed in dtex. This is the weight in grams of 10.000 metres of film. In one embodiment, the film according to the invention has a denier of at least 3000 dtex, in particular at least 5000 dtex, more in particular at least 10000 dtex, even more in particular at least 15000 dtex, or even at least 20000 dtex, in combination with strengths of, as specified above, at least 2.0 GPa, in particular at least 2.5 GPa, more in particular at least 3.0 GPa, still more in particular at least 3.5 GPa, and even more in particular at least 4.

The polyethylene films manufactured from the polyethylene obtained using the catalyst system of the present invention may be used in ballistic applications. This can be done, e.g., in accordance with what has been described in non-prepublished International patent application No. PCT/EP2009/052622, non-prepublished international patent application No. PCT/EP2009/055046, and non-prepublished European patent application No. 08160594.1, the descriptions of which are herewith incorporated by reference herein. They can also be used in ballistic materials known in the art, e.g., those described in WO97/00766, EP1627719, WO2007/122009,

WO2007/122010, WO2007/122011, WO2006/107197, WO2008/040506,
WO2008/040509, WO2008/040510, WO2008/040511.

The present invention will be elucidated by the following
5 examples, without being limited thereto or thereby.

Example 1

Four catalyst carriers were used, the properties of which are
10 presented in table 1.

Table 1

| Solid | BET S.A. (m²/g) | Particle size (nm) | Aldrich code |
|------------------|---------------------------------------|-------------------------------|---------------------|
| SiO ₂ | 590-690 | 5-15 | 637246 |
| ZrO ₂ | 100-120 | <100 | 572322 |
| TiO ₂ | 210 | <25 | 637254 |
| Hydroxyapatite | 9.4 | <200 | 677418 |

The carrier particles were treated with MAO solution (methyl
15 aluminoxane, 10%w in toluene) according to Cat. Comm 2008, 9,
1426, with some minor changes as described below. The powder
is dried at 100°C under vacuum for one night, then transferred
to the glove box for handling in an inert atmosphere. The
desired amount of solid (typically 1g) is placed in a Schlenk
20 tube, contacted with 5 ml of MAO solution and kept for 3h
under vigorous stirring. After that, the solid is filtered
(always keeping in inert conditions), washed with 4x10 mL of
fresh toluene and 4x10 mL of fresh heptane to remove unreacted
MAO and dried at room temperature under vacuum.

25 The solids obtained have been analyzed by means of SEM and EDX
in order to get information about the morphology and the
amount of Al present. The results are reported in Table 2 and
Figures 1 to 5.

Table 2

| Sample | S.A. (m ² /g) | Al ₂ O ₃ (%w) | MAO (as -Al(CH ₃)O-) (mmol/g) |
|------------------|-----------------------------|--|--|
| SiO ₂ | 590-690 | 20.58 | 4 |
| ZrO ₂ | 100 | 10 | 2 |
| TiO ₂ | 210 | 14 | 2.74 |
| Hydroxyapatite | 9.4 | 1.4 | 0.27 |

In the figures, Figure 1 shows ZrO₂ nanoparticles before (a) and after (b) MAO supportation. Figure 2 shows TiO₂ before (a) and after (b) MAO supportation. Figure 3 shows hydroxyapatite before (a) and after (b) MAO supportation. Figure 4 shows SiO₂ before (a) and after (b) MAO supportation.

Figure 5 shows EDX elemental analysis of support/MAO, with (a) showing the data for MAO on SiO₂, (b) showing the data for MAO on ZrO₂, and (c) showing the data for MAO on hydroxyapatite.

The amount of MAO on each solid appears to have a fairly direct relationship with the surface area. After that treatment, each solid has been tested in polymerization experiments as follows:

The desired amount of nanoparticles/MAO is placed in a Schlenk tube and contacted with a solution of the catalyst bis{2,4-ditertbutyl-6-[(2,3,4,5,6 pentafluorophenyl) imino]methyl}phenoxy}Ti dichloride, in a minimum amount of toluene (typically 1 mL) at room T and kept for 0.5-1h under vigorous stirring. In the meanwhile, a 1L flask, equipped with a mechanical stirrer, a gas inlet and outlet, a thermometer and a rubber cap, is filled with 0.5 L of solvent (typically toluene or heptane) and 2 mL of triisobutylaluminum (TibAl, 1M solution in hexane) are added to scavenge any impurities present. Then, 10mL of the resulting solution are transferred to the Schlenk tube containing the wet

nanoparticles/MAO/catalyst and the slurry is stirred for 5 additional minutes. During this time, the 1L flask is flushed with ethylene: when ready, the slurry is transferred to the flask by means of a cannula to start the reaction. The polymerization is run for 1h at the desired temperature, under constant ethylene flux and vigorous stirring (400rpm), and quenched with acidified methanol (95/5 v/v MeOH/HCl). The polymer is filtered out, washed with acetone and dried. Catalyst properties and polymerization results are reported in the following table 3.

Table 3

| Sample | Type | S.A. (m ² /g) | Amount (g) | MAO (mmol) | Cat(μmol) | Al _{MAO} /Ti | Ti/supp (μmol/m ²) |
|----------|------------------|--------------------------|------------|------------|-----------|-----------------------|--------------------------------|
| PE090206 | Hap | 9.4 | 0.38 | 0.10 | 12 | 9 | 3.4E+00 |
| PE081031 | SiO ₂ | 560 | 0.2 | 0.80 | 7.5 | 107 | 6.7E-02 |
| PE081121 | SiO ₂ | 560 | 0.24 | 0.96 | 22 | 44 | 1.6E-01 |
| PE090211 | TiO ₂ | 210 | 0.3 | 0.82 | 12.4 | 66 | 2.0E-01 |
| PE081127 | ZrO ₂ | 100 | 0.4 | 0.80 | 18.7 | 43 | 4.7E-01 |
| PE081128 | ZrO ₂ | 100 | 0.45 | 0.90 | 10 | 90 | 2.2E-01 |
| PE090216 | ZrO ₂ | 100 | 0.31 | 0.62 | 12.4 | 50 | 4.0E-01 |
| PE090304 | ZrO ₂ | 100 | 1.3 | 2.60 | 6.6 | 394 | 5.1E-02 |
| PE090309 | ZrO ₂ | 100 | 0.36 | 0.72 | 6 | 120 | 1.7E-01 |
| PE090126 | - | - | 0 | | 9 | 0 | |
| PE081215 | - | - | 0 | | 10 | 0 | |

| Sample | Solv | L | T (°C) | Yield (g) | Ox (%w) | Activity (Kg _{pol} /mol _{cat} *h*bar) | MAO (mmol/g) |
|----------|------|------|--------|-----------|---------|---|--------------|
| PE090206 | Hep | 0.20 | 20 | 1.1 | 35.8 | 57 | 0.27 |
| PE081031 | Tol | 0.10 | 20 | 1.6 | 12.7 | 183 | 4 |
| PE081121 | Tol | 0.50 | 27 | 5.0 | 4.8 | 216 | 4 |
| PE090211 | Hep | 0.20 | 13 | 4.9 | 6.2 | 367 | 2.74 |
| PE081127 | Tol | 0.50 | 15 | 4.2 | 9.5 | 203 | 2 |
| PE081128 | Hep | 0.15 | 14 | 3.9 | 11.5 | 348 | 2 |
| PE090216 | Hep | 0.20 | 13 | 2.0 | 15.5 | 136 | 2 |
| PE090304 | Hep | 0.50 | 24 | 6.1 | 21.4 | 723 | 2 |
| PE090309 | Hep | 0.20 | 12 | 2.0 | 18.0 | 273 | 2 |
| PE090126 | Hep | 0.2 | 13 | 0.0 | 0.0 | 1 | - |
| PE081215 | Tol | 0.2 | 13 | 0.3 | 0.0 | 28 | - |

Most of the samples have been analyzed by DSC. Figure 6 shows a first melting T of 140C.

Rheology experiments conducted on polyethylenes synthesised using the supported catalytic system are given in figure 7: they show the modulus build-up typical of disentangled polymer; drawing experiments conducted on most of the samples show easy drawability of PE-films confirming that the disentangled character of the polymer is retained even when using a supported catalytic system.

Figure 8 reports the polymerization activity (in KgPE/molcat*h*bar) versus the Ti/support (micromol/m²): a reasonable hypothesis to justify the trend is that the activation of the catalyst is better when a larger surface (and so a higher MAO content) is available. This could also fit with the observation that the results from silica-supported system are not in the trend, probably because the smaller pores on the surface are not able to give a good 'environment' for the catalytic system (not easily accessible to monomer).

Samples PE081215 and PE090126 (see table 3 above) have been performed in order to estimate the polymer formed by potential catalyst leaching from the surface and interacting with TiAl. The reaction in toluene gave a low activity, and the polymer obtained was analyzed by DSC (Figure 9), the lower melting temperature suggests that the sample is different from the UHMWPE obtained with the supported catalytic system. The reaction in heptane gave almost no polymer at all: the solubility of catalyst and MAO in this solvent is very small, so the leaching process should not be a major concern when using it.

Example 2

A variation on Example 1 was carried out by supporting MAO on carrier particles which were subjected to ultrasonication before or during application of the MAO and prior to contact with catalyst. The supported materials were used in polymerisation in the same manner as described in Example 1 above. In Table 4 are reported the polymerization results

10

Table 4

| Sample | Type | S.A. (m ² /g) | Amount (g) | MAO (mmol) | Cat(μmol) | Al/Ti | Ti/supp (μmol/m ²) |
|----------|------------------|--------------------------|------------|------------|-----------|-------|--------------------------------|
| PE090424 | Hap | 9.4 | 0.33 | 0.18 | 8.8 | 21 | 2.8E+00 |
| PE090401 | TiO ₂ | 200 | 0.45 | 1.23 | 18 | 69 | 2.0E-01 |
| PE090402 | TiO ₂ | 200 | 0.3 | 0.82 | 11 | 75 | 1.8E-01 |
| PE090330 | ZrO ₂ | 100 | 0.8 | 2.00 | 7.5 | 267 | 9.4E-02 |
| PE090408 | ZrO ₂ | 100 | 0.3 | 0.75 | 11 | 68 | 3.7E-01 |

| Sample | Solv | L | T (°C) | Yield (g) | Ox (%w) | Act | MAO (mmol/g) |
|----------|------|------|--------|-----------|---------|-----|--------------|
| PE090424 | Hep | 0.20 | 13 | 3.0 | 11.0 | 303 | 0.56 |
| PE090401 | Hep | 0.50 | 8 | 7.6 | 5.9 | 397 | 2.74 |
| PE090402 | Hep | 0.50 | 9 | 7.8 | 3.8 | 682 | 2.74 |
| PE090330 | Hep | 0.50 | 7 | 3.9 | 20.5 | 413 | 2.5 |
| PE090408 | Hep | 0.20 | 12 | 3.0 | 10.0 | 245 | 2.5 |

For zirconia, application of ultrasonication resulted in an increase of the quantity of supported MAO from 2 mmol/g to 2.5 mmol/g, and an increase in the activity from 136 kg/molcat*h*bar to 245 kg/molcat*h*bar (referred to experiments PE090216 and PE090408 repeated in same conditions apart from sonication). For titania, even if the absolute quantity of supported MAO remained the same (2.74mmol/g), the activity went up from 360 kg/molcat*h*bar to 600 kg/molcat*h*bar. For hydroxylapatite, the quantity of

20

supported MAO increased from 0.27 to 0.56 mmol/g and activity increased from 57 to 303 kg/molcat*h*bar.

Figure 10 shows MAO supported on hydroxyapatite (left) and resulting PE (right) Figure 11 shows MAO supported on TiO₂ (left) and resulting PE (right). Figure 12 shows MAO supported on ZrO₂ (left) and resulting PE (right).

Example 3

10

A catalyst was prepared as described in Example 1. The catalyst contained 0.2 micromol catalyst/m² support. The titania particles had an average diameter of below 25 nm.

15

The catalyst was used in PE manufacture as described in Example 1, with the variation that a 10L polymerization reactor was used. The polymerization vessel was charged with 5L of solvent (heptane), thermostated at the desired temperature and saturated with ethylene at 1 bar gauge. When ethylene saturation was achieved, the supported catalyst was injected and the polymerization was kept under vigorous stirring (400 rpm) at constant temperature and pressure for the required time (1h). The resulting PE is estimated to have an Mw of 4 million g/mol an elastic shear modulus directly after melting of 1.29 GPa.

25

The polyethylene was subjected to solid state processing as follows:

30

25 gram polyethylene synthesized as above was compacted at an average pressure of 140 bar at a maximum temperature of 130°C maintained for 10 minutes (cooling of the compacted sheet was carried out while maintaining the pressure at 140 bar). The

resulted sheet was 1.4 mm thick, 610 mm long and 30mm wide. Its density was 1.0 g/cm³. The sheet was pre-heated to 125°C and subjected to a rolling-stretching step to form a film. Based on the dimensional changes, the ratio of elongation of the integrated rolling/stretching process was 11.4. The surface temperature of the roller-set was 130°C. The compacted sheet was subjected to a stretching step at 140°C into three consecutive steps that lead to a total draw ratio of nearly 290. The total draw ratio (TSRM) was determined by mass per unit length of the film before and after drawing. The results are given in Table 5 below.

Table 5

PE100409FI11GF (on TiO₂ support, ~3.5%)

| TRSM | thickness µm | width mm | Tensile strength GPa | Modulus GPa | BEsp J/g | Elongation at break % |
|-------|-----------------|-------------|----------------------------|----------------|-------------|-----------------------------|
| 13.0 | 210.0 | 17.3 | 0.48 | 13.5 | 10.71 | 3.66 |
| 44.7 | 130 | 9.30 | 1.10 | 70.9 | 13.91 | 1.78 |
| 136.5 | 73 | 5.85 | 1.85 | 127.8 | 20.69 | 1.74 |
| 191.4 | 62 | 5.05 | 2.12 | 145.7 | 24.29 | 1.77 |
| 291.3 | 51 | 4.35 | 2.15 | 156.5 | 24.25 | 1.65 |

In the table BEsp stands for energy at break. TRSM stands for total draw ratio based on mass as described above. The tensile strength and modulus data in GPa have been converted from the data in N/tex using a density of 0.95 gram/cm³. The modulus in Table 5 is the segment modulus determined by taking the slope of stress-strain curve obtained during deformation of the tape (length 100mm, drawing speed of 50mm/min) at room temperature. As can be seen from Table 5, the polyethylene prepared by the process of the present invention can be processed to form a film with good properties.

Claims

1. Process for manufacturing an ultra-high molecular weight polyethylene, wherein olefin monomers are contacted with a catalytic system under polymerisation conditions under formation of a polyethylene, wherein the catalytic system comprises an active component on a particulate carrier in a site density in the range of $5 \cdot 10^{-9}$ to $5 \cdot 10^{-6}$ mole of catalytic sites per m^2 of carrier surface area, the particulate carrier having an average particle diameter in the range of 1-300 nm, wherein the polyethylene has a weight average molecular weight (Mw) of at least 500 000 gram/mole, and an elastic shear modulus G_N^0 , determined directly after melting at 160°C of at most 1.4 MPa.
2. Process according to claim 1, wherein the UHMWPE has a molecular weight between $1 \cdot 10^6$ gram/mole and $1 \cdot 10^8$ gram/mole.
3. Process according to claim 1 or 2, wherein the UHMWPE has an elastic shear modulus determined directly after melting of at most 1.0 MPa, still more in particular at most 0.9 MPa, even more in particular at most 0.8 MPa, and even more in particular at most 0.7 MPa.
4. Process according to any one of the preceding claims wherein the UHMWPE has a Mw/Mn ratio of at most 6, more in particular at most 4, still more in particular at most 3, even more in particular at most 2.
5. Process according to any one of the preceding claims which comprises an active component on a particulate carrier, characterised in that the average number of catalytic sites per carrier particle is in the range of 1 to 1000, more in particular in the range of 1 to 500.

6. Process according to any one of the preceding claims, wherein the particulate carrier has an average particle diameter in the range of 1-200 nm, more in particular 1-100 nm, still more in particular 1-50 nm, even more in particular
5 1-20 nm.
7. Process according to any one of the preceding claims wherein the catalytic system comprises an activator compound and a metallocene or post-metallocene compound wherein at
10 least one of the activator compound and the metallocene compound is present as active component on the particulate carrier.
8. Process according to claim 7, wherein the activator
15 compound is immobilised on the particulate carrier.
9. Process for manufacturing a polyethylene film, which comprises subjecting a starting polyethylene to a compacting step and a stretching step under such conditions that at no
20 point during the processing of the polymer its temperature is raised to a value above its melting point, wherein the starting polyethylene has a weight average molecular weight (Mw) of at least 500 000 gram/mole, and an elastic shear modulus G_N^0 , determined directly after melting at 160°C of at
25 most 1.4 MPa, and is obtained by the process of any one of the preceding claims.
10. Process according to claim 9 wherein the stretching step is carried out in such a manner that the total stretching
30 ratio obtained is at least 50, in particular at least 70, more in particular at least 90, still more in particular at least 120, in particular at least 140, more in particular at least 160.

Figure 1(a)

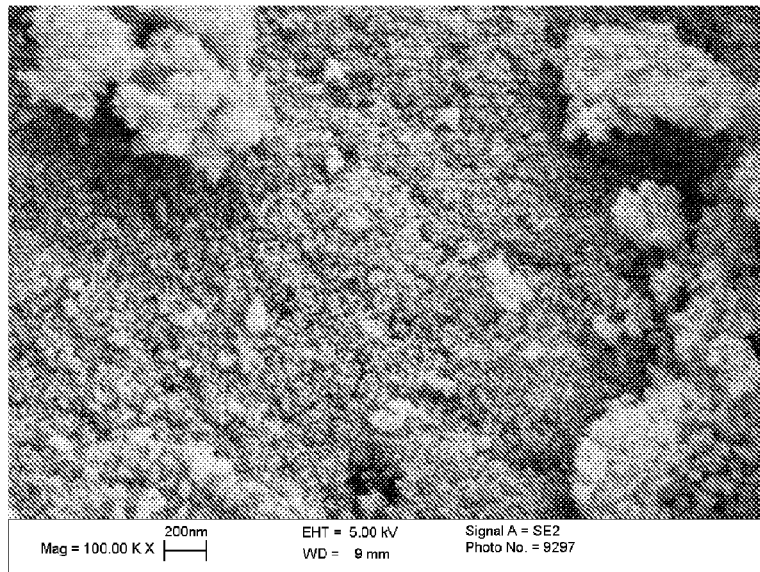


Figure 1(b)

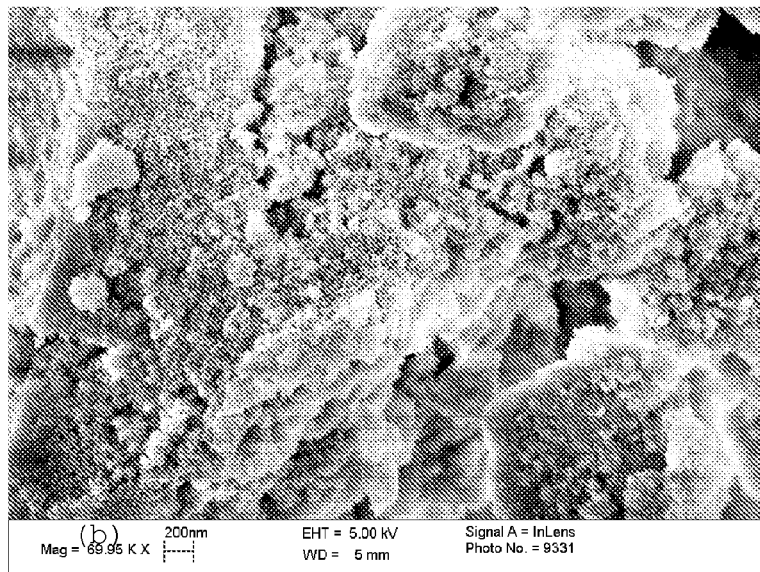


Figure 2 (a)

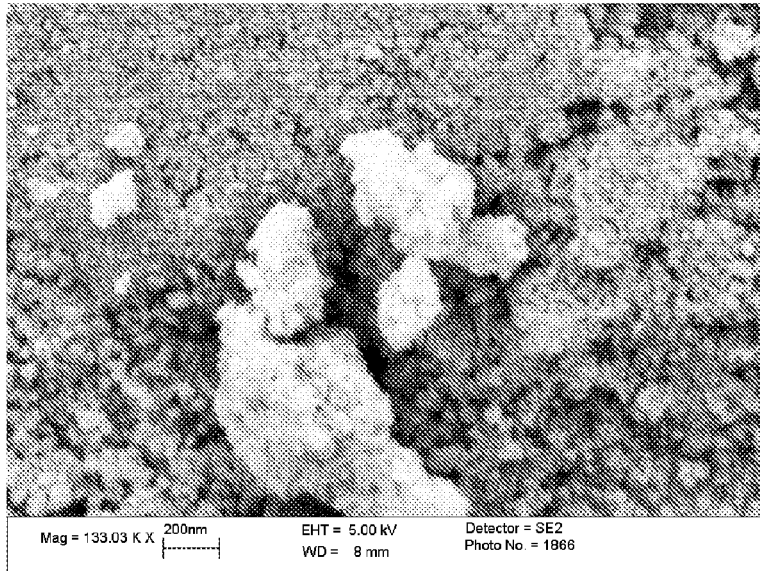


Figure 2 (b)

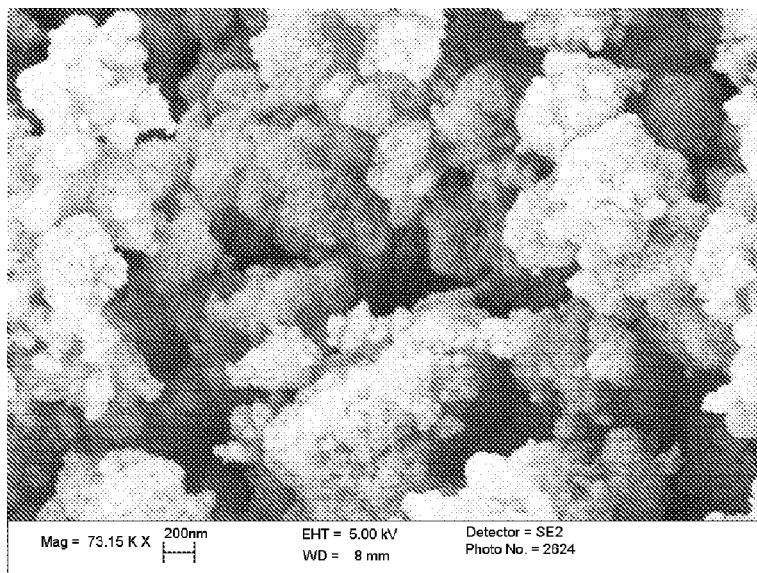


Figure 3 (a)

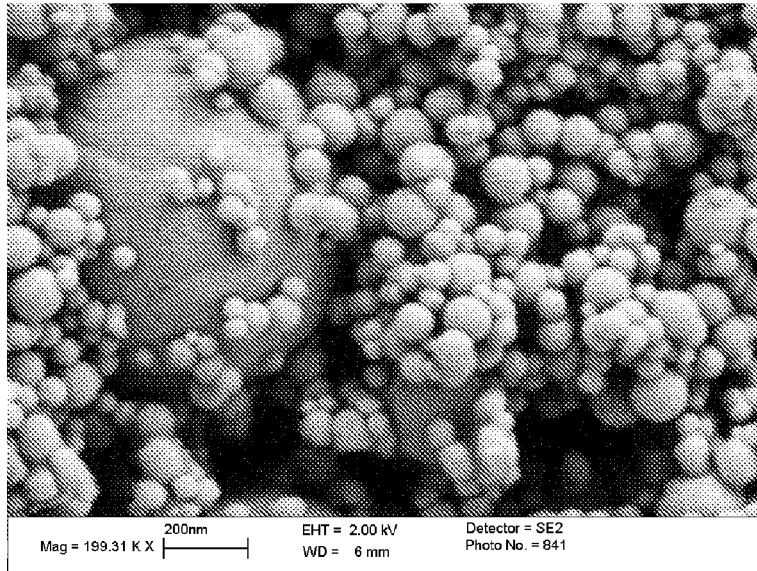


Figure 3 (b)

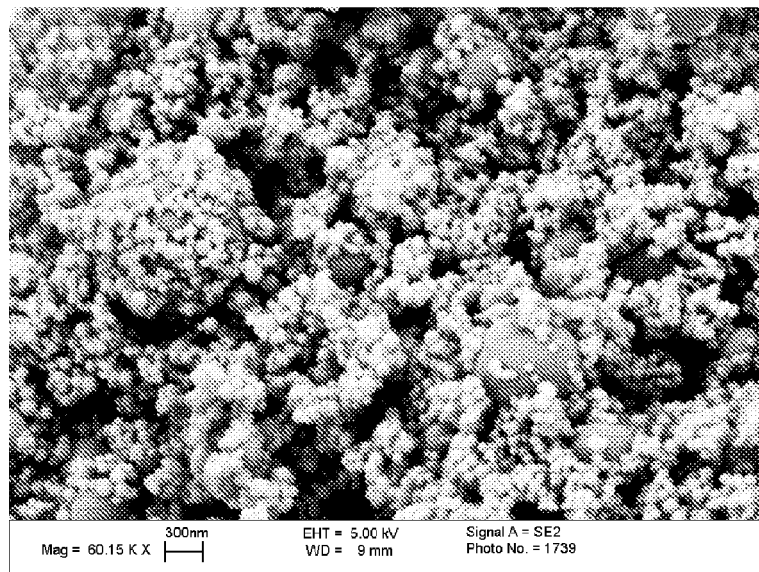


Figure 4(a)

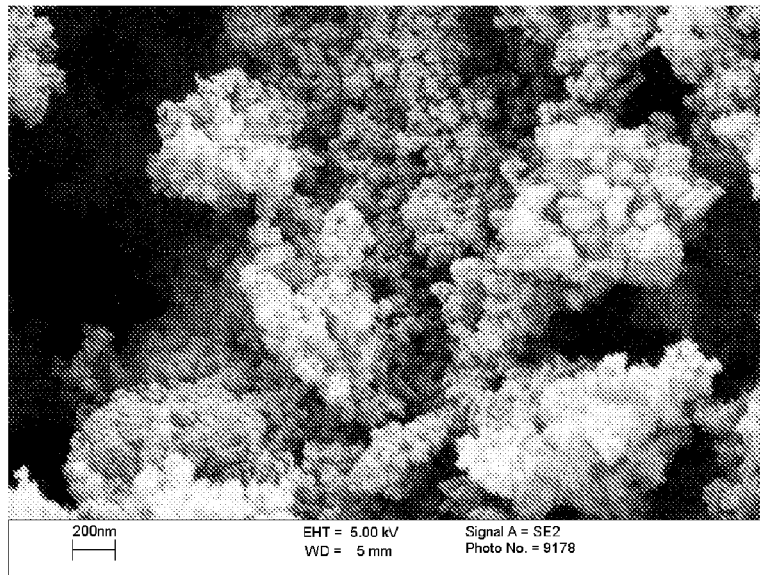


Figure 4(b)

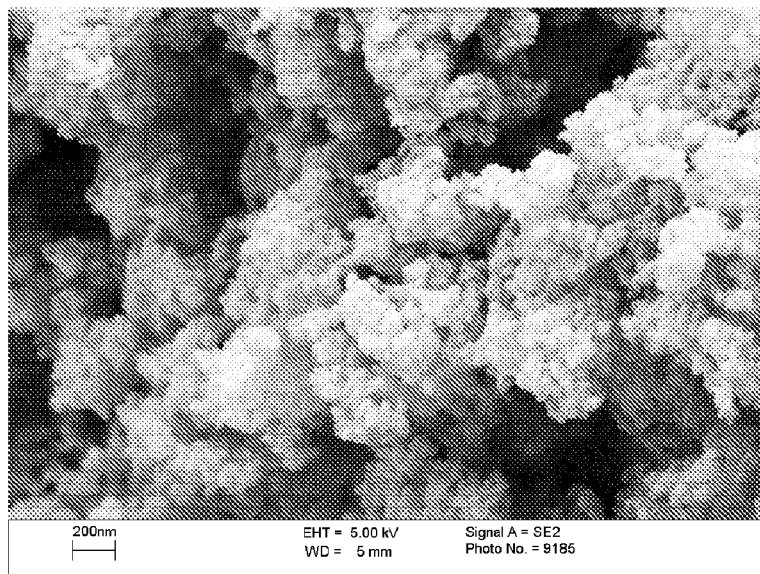
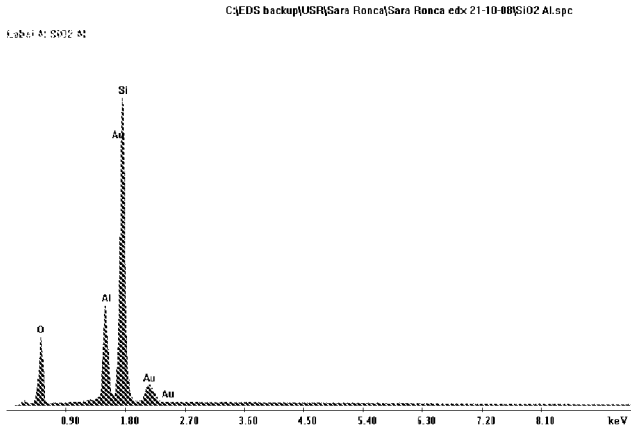
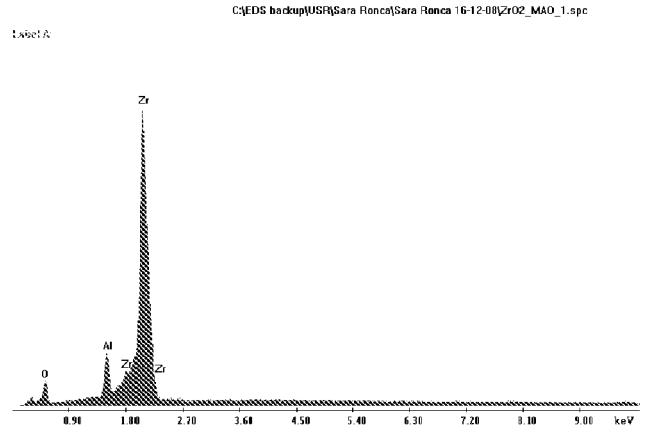


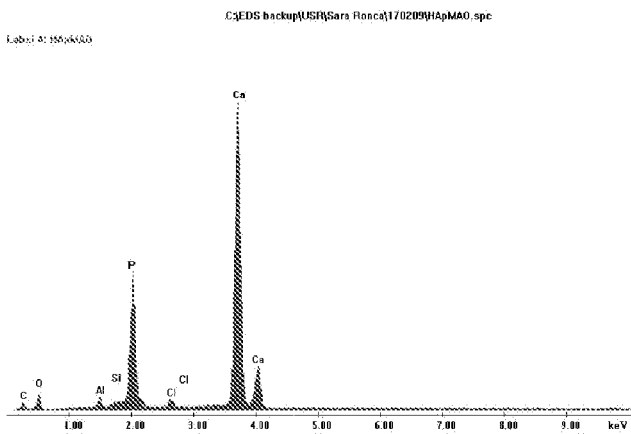
Figure 5



SiO2/MAO



ZrO2/MAO



Hydroxyapatite/MAO

Figure 6

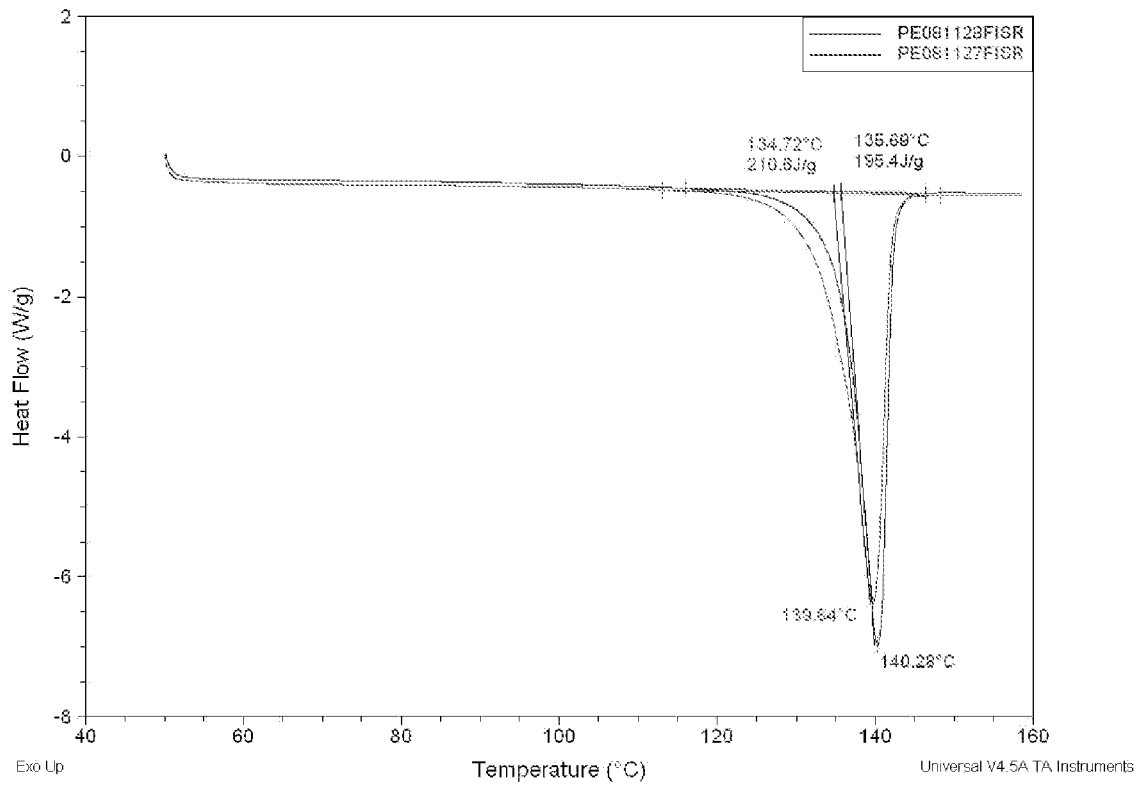


Figure 7

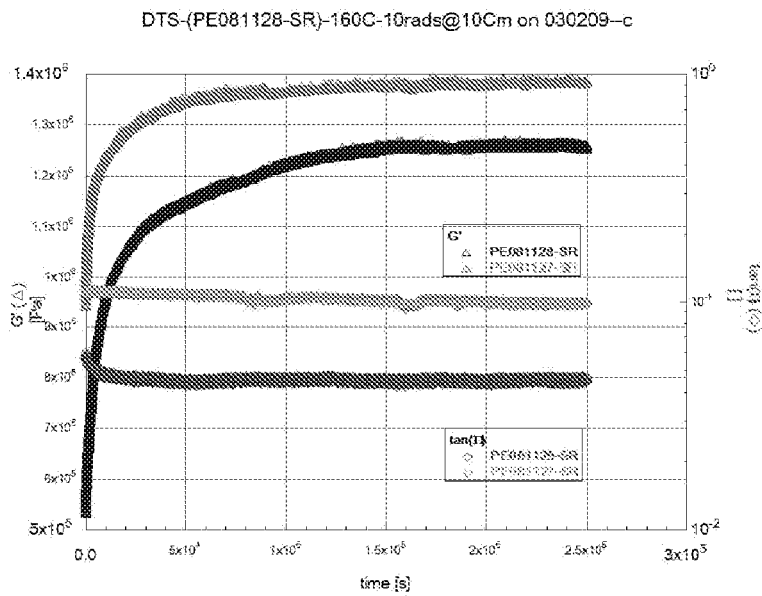


Figure 8

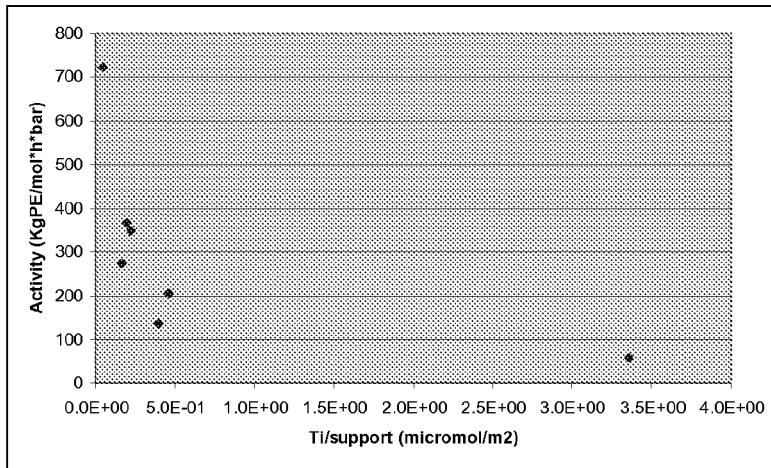


Figure 9

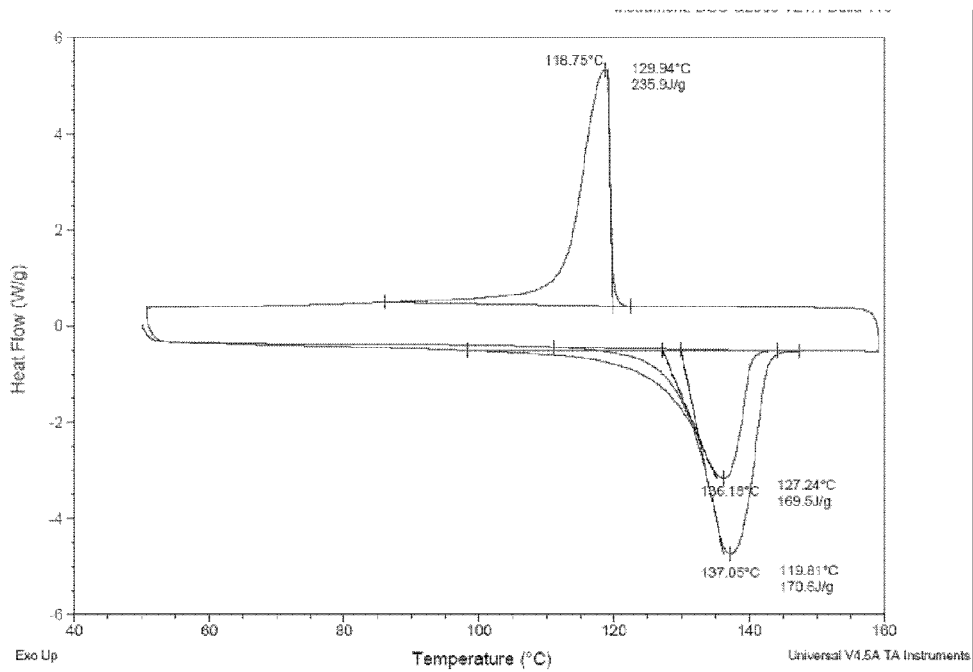


Figure 10

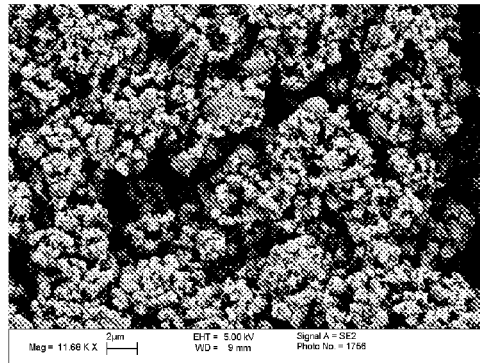
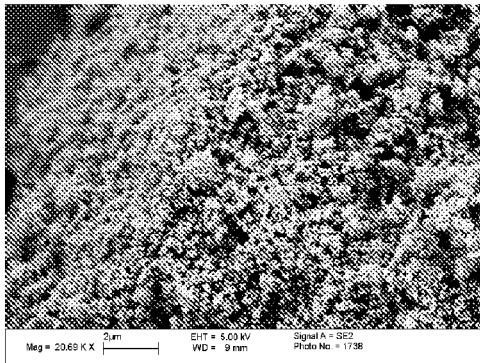


Figure 11

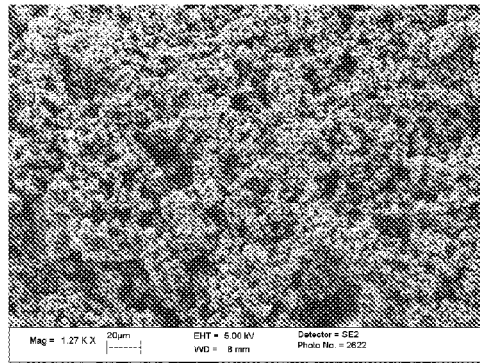
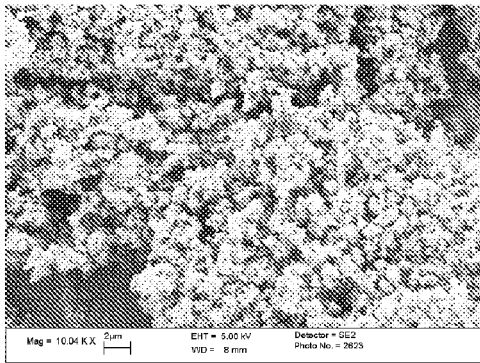
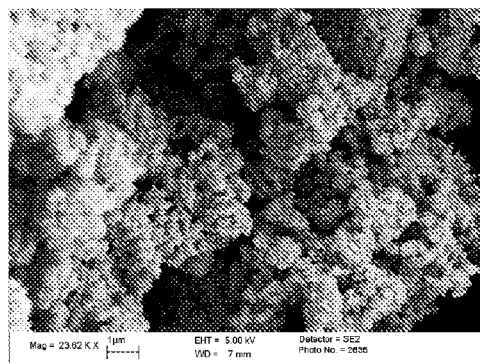
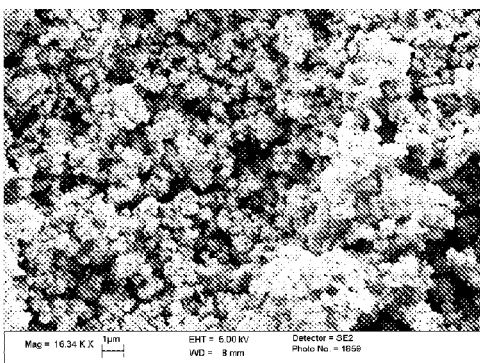


Figure 12



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2010/057697

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08F4/64 C08F10/02
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuation of Box C.

See patent family annex.

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Date of the actual completion of the international search

9 September 2010

Date of mailing of the international search report

15/09/2010

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Fischer, Brigitte

INTERNATIONAL SEARCH REPORT

Information on patent family members

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| International application No PCT/EP2010/057697 |
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