Abstract: Described is a method for the preparation, by the underwater pelletizing technique using a die having a diameter of at most 1.2 mm, of polyester or polycarbonate particles having a particle size of 1.3 mm or less, to particles obtainable by the said method, to a collection of such polymer particles, to the uses of such particles.
Method for the preparation of polymer comprising particles

The present invention relates to a method for the preparation of particles comprising at least a polymer, wherein a melt comprising the said polymer is extruded by passing the melt through at least a die into a solidifying medium having a temperature of below the melting temperature of the melt, allowing the melt to solidify in the solidifying medium into the particles. The invention further relates to particles obtainable by the said method, to a collection of such polymer comprising particles, and to the use of such particles.

Background of the Invention

Polymeric particles, in particular for use in fracturing of subterranean formations in oil and gas production are known. Particles such as the said particles are also known as 'proppants'. Proppants are incorporated into high-pressure fluids to help create and maintain fractures in rock, contributing to increased well production in the oil and gas field.

Proppants are particulate material used in the hydraulic fracturing of subterranean formations, and they also function to keep the cracks open. In the art, sand and small ceramic beads are suspended in the fracturing fluid and often used in hydraulic fracturing of oil and gas wells. Hydraulic fracturing is accomplished by pumping fluid down a well under high pressure to create fractures in the surrounding rock. The proppants flow into the fractured cracks and extend outward from the wellbore to prop the fractures open. After pumping, the proppant materials remain in the cracks of the separated rock and form an open channel to allow the hydrocarbons to flow more easily to the surface. As oil and gas resources continue to deplete, there is more need for hydraulic fracturing. Fracturing may also be accomplished by the use of explosive charges and in such applications proppants may also be used.

A number of considerations are taken into account when selecting proppants appropriate to the intended use such as particle size. It is often useful to have sufficient space between the proppant particles for the desired fluid to be able to easily flow between them. In addition, the size of material may also be a consideration depending on depth of field applications. For shallow depths big round particles (i.e. having a diameter of above 1.0 mm) can be favoured, while for deeper depths smaller round particles (i.e. having a diameter of 0.4 - 0.8 mm or smaller) can be the material of choice.

The cracks, once formed, tend to reclose as a result of the enormous pressure within the geologic formations. Therefore, the particles should also be resistant to so-called "closure stress" and should preferably retain their shape and integrity at the temperatures at which hydraulic fracturing takes place. The said temperatures are herein also referred to as Operational temperatures'. When particles are crushed, they can form very fine particles that decrease the permeability of oil or gas through the cracks. The hardness and resistance to
deformation are therefore also essential to support the burden of the rock, and proppants should have the strength to resist the stress. Regarding the above, the particles should preferably have a compressive strength of at least 45 N/mm² at a temperature of at least 80°C, preferably at the temperature at which hydraulic fracturing takes place, to resist the closure stress within the cracks.

At shallow depths, the minimal temperature at which hydraulic fracturing takes place is often about 60°C. Temperatures of 150°C or higher are an issue at deeper depths. Materials having sufficient compressive strength at the temperature at which hydraulic fracturing takes place should be selected.

Regarding the above the size and the compressive strength at the operational temperature are important properties.

Among materials commonly used as proppants are sand, ceramic beads, and walnut hulls. However one of the problems using sand or ceramics is that the density of the proppant particles is high compared to the fracturing fluid. For example, while the density of a typical fracturing fluid is about 1.0 g/ml, the density of sand is about 2.65 g/ml. As a result the proppant particles settle too rapidly during the fracturing process. Therefore fracturing fluids often have high viscosities in order to effectively suspend such high specific gravity proppants. A disadvantage to using high viscosity fluids is that they often do not efficiently penetrate small cracks.

The above materials, while possessing the strength desired for effective use as a proppant, also deteriorate into fines under the pressure that would be experienced underground. Another problem is that proppants such as walnut hulls do not possess the required resilience needed to press back against shifting subterranean pressures.

US201/0/0285998 describes the preparation of polyamide beads having a particle size of between 1.25 - 1.5 mm. Thereto, the polymeric melt of the polyamide is extruded through a die, cut into pieces and allowed to solidify in water. As the die opening and the cutting both take place in the water, this technique is also known as underwater pelletizing. The problem of this technique, in particular with polymers having a high melting point, is the risk of solidification of the melt at the die opening, resulting in closure of the die. Therefore, the minimal size of the die opening is limited. According to US201/0/0285998, the die opening is heated to 345-389°C to minimize such clogging, allowing smaller die openings of 0.8 - 1.2 mm. Although the underwater pelletizing technique is used for the preparation of small spherical and round particles, the particles of US201/0/0285998 are still rather large (1.25 - 1.5 mm), despite the rather small die openings. Further, the particles obtained are ellipsoidal without concave portions. However, it has not been possible to produce particles of having a roundness and sphericity of 0.7 or higher. Further, particles having a smaller size than 1.25 mm could not be obtained.
It is therefore an object of the invention, to provide polymeric particles, i.e. particles consisting of a polymer or mixture of polymers, or having a matrix of such a polymer or polymers with fillers and/or other additives, which particles have a small particle size of below 1.3 mm and having improved roundness and sphericity.

Therefore, in the art there is a great need for polymeric proppant materials that have as polyamide a density close to that of water, but having a smaller size and having improved roundness and sphericity.

The present inventors have surprisingly found that proppants having the required properties can surprisingly be produced by starting from polymeric material that comprises at least a polymer, chosen from the group, consisting of a polyester (PE) a polycarbonate (PC) or a mixture thereof. The above problems are therefore solved or less pronounced by providing the method as defined in claim 1.

Without the intention to be bound to any explanation, it is believed that the viscosity of the melt of the polyamide of US201/0/0285998 is significantly higher than that of the melts used in the method of the present invention. This higher viscosity has a significant deteriorating effect in the production process, as clogging of the die holes still take place, and the melt tends not to solidify in round and spherical shape, but more or less in ellipsoid, banana-like shapes, which are undesired.

However, it was surprisingly observed that using polymeric melts, based on polyester or polycarbonate, clogging was significantly less, allowing the production of particles of even smaller size, and very surprisingly, resulting in particles of virtually perfect roundness and sphericity.

According to the invention, the melt may also comprise other polymers as additives. However, the melt preferably comprises at least 40 w/w%, based on the total polymer content of the melt polyester and/or polycarbonate, more preferably at least 50 w/w%, even more preferably at least 60, 70, 80, 90 or more w/w%.

Polyesters and polycarbonates that are suitable as proppant according to the invention usually have a high melting point \( T_{pm} \) (the peak melting temperature as determined according to the ISO standard 11357-1 :1997), e.g. significantly higher than that of water. As a result the melt will solidify instantly upon contact with the water.

The term 'control of the temperature of the melt at the die opening such, that closure of the die outlet opening by solidification of the melt at the die outlet opening is reduced' means that the closure of the die at the outlet opening is less than under the same process conditions without the said temperature control. Preferably, the said solidification is avoided.

By the above method particles comprising at least a polymer having a density of 1.0 to 2.1 g/ml, a particle size of 1.3 mm or less and optionally a compressive strength of at least 45 N/mm² at 80°C having improved roundness and sphericity can be produced for the very
first time. Unless indicated otherwise, the term 'particle size' as used herein reflects the weight based particle size, which equals the diameter of the sphere that has same weight as a given particle. The weight based particle size is defined by the following formula:

\[ \text{weight (particle)} = \frac{3 \times \text{weight (particle)}}{4 \times \pi \times \text{density (particle)}} \]

\[ ^{1/3} \]

The skilled person will be capable to choose the proper polymer or a combination of polymers that have the proper density and compressive strength in solid state. The compressive strength can be determined using e.g. apparatus from the company Instron type 3366 and following the manufacturer's manual. Herein the compressive strength is measured at the indicated temperature on a single particle at a compression of the particle of 20% (i.e. compressed to 80% of its original diameter).

In coming to the invention the inventors overcame the prejudice against the use of polymeric proppants. It has been encountered by the inventors that using the commonly known underwater granulation techniques clogging of the outlet opening of the dies could not be avoided for suitable polymers, as soon as a small particle size, e.g. below 1.3 mm, in particular below 1.2 mm and below 1.1 mm was envisaged. However the inventors found that solidification of the melt at the die outlet opening could be avoided by controlling the temperature of the melt at the outlet opening of the die. The term 'controlling' includes transferring heat to the melt at the location of the die outlet opening or reducing the loss of heat from the melt at the position of the die outlet opening to the solidifying medium, therewith avoiding clogging of the die outlet opening.

There appeared to be some compensation possible by elevating the pressure or temperature of the melt. However it was found that using the conventional underwater granulation techniques at the required small diameters of the die outlet opening resulted, in most cases, in clogging of the die outlet opening by solidified polymer. Additional control appeared to be necessary, which is explained further below.

In an attractive embodiment said controlling of the temperature of the melt at the die outlet opening comprises holding the temperature of the said die, at least at the outlet opening thereof, at a temperature higher than 60°C below the melting temperature \( T_{pm} \) of the polymer, i.e. at a temperature above \( (T_{pm} - 60°C) \).

It was found that the die outlet openings did not anymore clog and that the obtained polymer comprising particles appeared to be very well suitable as small sized proppant particles (i.e. having a particle size of 1.3 mm or less, preferably 1.2 mm or less, more preferably 1.1 mm or less, 1.0 mm or less, still even more preferably between 0.4 and 0.8 mm, and most preferably between 0.4 and 0.6 mm). It appeared that using the conventional underwater granulation techniques, the temperature of the outlet opening was too low to avoid clogging. By holding the temperature at the above values, clogging could surprisingly be avoided, enabling, for the first time, the production of small sized polymer-based
proppants, smaller than obtained for polyamide-based particles.

The term particle comprises particles of any shape, such as spherical, spheroidal, elliptical, and right cylindrical shapes. Spherical shapes are preferred as these have the best flow properties in the fracturing fluid.

It is however advantageous to use a single polyester or polycarbonate polymer as the polymer with the least qualities usually determines the properties of the particle.

Herein, the term 'the polymer' also encompasses a cross-linked polymer, a cross linked copolymer, a cross linked terpolymer, a cross linked block(co) polymer or any mixtures thereof unless indicated otherwise. As defined above, the polymer is chosen from the group consisting of polyesters and polycarbonates. The particle can also advantageously comprise one or more filler materials, e.g. to adjust the specific weight of the particle, to reinforce it, or to reduce costs of the particle material.

Preferably the melting temperature $T_{pm}$ of the polymer is at least 120°C, preferably at least 150°C, more preferably at least 180°C, most preferably at least 200°C. Polymers having a relatively low melting point usually appear to be less suitable as component for the polymer comprising particles according to the invention. Further, particles of such polymer materials would easily melt at the temperatures at which fracturing takes place.

In addition to the above-mentioned compressive strength, an additional parameter for the determination of the temperature dependent integrity is the softening point, expressed as the so-called VICAT softening point, according to ISO standard 306. For a polymer to be suitable as proppant material, the polymer should preferably have a softening point that is above the lowest temperature at which hydraulic fracturing takes place. If the softening point is too low, the proppant particles will be soft during the hydraulic fracturing, therewith loosing their shape and not having the pressure resistance needed to keep the fractures open.

Preferably the polymer has a VICAT softening point of at least 50°C, preferably at least 70°C. A softening point in the said ranges is advantageous, as at the working temperatures during fractioning, the particles preferably remain rigid, although some deformation may take place.

Preferably in step a) the temperature of the melt is at least 180°C, preferably at least 200°C, more preferably at least 230°C, most preferably at least 260°C. The temperature of the melt also has an impact on the temperature of the die. A higher temperature of the melt assists in holding the temperature of the die at the required level. Further, the processability at higher temperatures is improved, as the viscosity of the melt will be lower. A too high temperature will however result in degradation of the polymer in the melt. The temperature of the melt is therefore preferably below 400°C.

Also in step a) the temperature of the melt is at least 20°C above the melting temperature $T_{pm}$ of the polymer, preferably 30°C above the melting temperature $T_{pm}$ of the
polymer, more preferably 40°C above the melting temperature $T_{pm}$ of the polymer in order to avoid clogging of the melt at the die.

In another embodiment the temperature of the solidifying medium is at 50°C or more lower than the melting point of the polymer, preferably 60°C or more lower than the melting point of the polymer. The temperature of the solidifying medium is preferably 100°C or less lower, preferably 80°C or less lower than the melting point of the polymer. By choosing the temperature of the solidifying medium accordingly, the temperature difference between the melt and the solidifying medium is large enough to allow a good solidification of the melt, without allowing the melt to cool off too much at the location of the die outlet opening, therewith avoiding clogging of the said outlet opening.

Preferably the temperature at the outlet opening of the die is held at a temperature higher than 40°C below the melting temperature $T_{pm}$ of the polymer (i.e. $T_{pm} - 40°C$), preferably higher than 20°C below the said melting temperature $T_{pm}$ (i.e. $T_{pm} - 20°C$), more preferably at the said melting temperature $T_{pm}$; even more preferably at least 20°C, still even more preferably at least 30°C above the melting temperature $T_{pm}$ of the polymer. The higher the temperature at the outlet opening, the less chance for clogging of the die outlet opening exists. Care has to be taken that the temperature does not exceed the decomposition temperature of the polymer in the melt. Preferably the temperature at the outlet opening of the die is held at a temperature of lower than 100°C above the melting temperature $T_{pm}$ of the polymer, preferably lower than 100°C above the melting temperature $T_{pm}$ of the polymer.

In another preferred embodiment the temperature at the outlet opening of the die is held at above the melting onset temperature $T_{im}$ of the polymer. The $T_{im}$ of the polymer is also defined in the above ISO 11357-1 1997 standard and indicates the temperature where melting of the polymer starts. It is commonly known that polymers do not have a definite melting point but a melting range, starting at the onset temperature, here and in the ISO 11357-1 1997 standard indicated by $T_{im}$, and ending at the end temperature indicated in the ISO 11357-1 1997 standard indicated by $T_{fm}$. The melting point $T_{pm}$ is located between $T_{fm}$ and $T_{pm}$, as indicated in the said standard.

In an attractive embodiment of the present invention the temperature of the die, at least at the outlet opening thereof, is held by transferring external heat to the die, or by generating heat in the die. In underwater granulation the solidifying medium lowers the temperature of the die at the outlet opening thereof. By the term 'controlling the temperature of the melt at the die outlet opening' is meant that the temperature of the melt, in particular at the outlet opening of the die, is controlled such that no clogging takes place. Although the temperature of the melt may be high, the temperature of the die at the outlet opening thereof is usually not sufficient to avoid clogging of the outlet opening by the melt. Therefore external heat can be transferred to the melt e.g. through the die, in particular at the outlet opening
thereof or heat can be generated in the die, such that the temperature is sufficient to heat the melt at the outlet opening of the die such, that clogging is avoided.

The temperature of the die, at least at the outlet opening thereof is preferably held by transferring external heat to the die by arrangement of at least a channel in the die, located in the vicinity of the die outlet opening and transporting of a heat exchange medium through the said channel, by heat induction of the die at the location of the outlet opening or by the temperature of the solidifying medium or a combination thereof. By arranging one or more heat exchange channels in the die enabling heat to be exchanged from a heat-exchanging medium to the die at the outlet opening, clogging of the melt at the outlet opening can be avoided. A preferred heat exchange medium comprises oil or glycol, but any other organic liquid or mixture thereof capable of transferring heat at a temperature of above 100°C, preferably above 150°C, more preferably above 180°C is suitable as long as clogging of the outlet opening is avoided. An example of such an arrangement where hot oil is heating the die opening is described in EP0305862, herein incorporated by reference. The die can also be designed such, that heat can be generated by heat induction within the die. Another attractive embodiment to reduce heat loss at the die outlet opening, at least to the outlet opening thereof, is by increasing the temperature of the solidifying medium. In case water is used, the maximum temperature of the said solidifying medium is 100°C (or alternatively the system could be operated under pressure to increase the boiling temperature of water accordingly). This can however be insufficient to hold the temperature of the die at the outlet opening at the required value to avoid clogging. Additional heat transfer would be needed in most cases.

Preferably the temperature of the solidifying medium is above 50°C, preferably above 90°C, more preferably above 120°C, even more preferably above 140°C. As indicated above, the temperature of the solidifying medium can be used to hold the temperature of the die at the outlet opening at the required level to avoid clogging. In case a temperature of more than 100°C is desired, another solidifying medium than water should be contemplated, as long as the said medium is inert to the melt and the solidified particles.

Preferably the temperature of the solidifying medium is below 250°C, preferably below 200°C. Higher temperatures may have a negative impact on the solidifying process of the melt, resulting in less reproducibility with regard to particle size. However, if polymeric melts having a high melting point are used, the temperature of the solidifying medium can be accordingly elevated.

The atmospheric boiling point of the solidifying medium is therefore preferably above 90°C, more preferably above 100°C, even more preferably above 110°C, still more preferably above 120°C, most preferably above 150°C.

The solidifying medium is preferably chosen from the group consisting of water, liquid
salt, or an organic liquid or any mixture thereof.

The solidifying medium preferably comprises an organic liquid, having an atmospheric boiling point of above 90°C, more preferably above 100°C, even more preferably above 110°C, still more preferably above 120°C, most preferably above 150°C.

In an attractive embodiment, the solidifying medium is inert to the melt and the particles. With 'inert' is meant that the melt and the solidified particles do not dissolve substantially in the solidifying medium. Apolar organic liquids may therefore be less suitable, as these liquids tend to dissolve the melt.

Preferably, the solidifying medium comprises a polar organic liquid. More polar organic liquids are in general more inert for many polymers as compared to less polar organic liquids. In another attractive embodiment, the solidifying medium comprises a mixture of two or more organic liquids, or a mixture of one or more organic liquids with water.

The polar solidifying medium preferably comprises an alcohol, ether, acid or ester. Among suitable alcohols are aliphatic alcohols like octanol with a boiling point of 195°C and decanol with boiling point 220-235°C. Also glycols can be used e.g. propylene glycol with boiling point 188°C and ethylene glycol with boiling point 197°C. In general also ethers can be used, but these are less preferred because of the relatively low boiling point and tendency to react with oxygen to form peroxides and explosive mixtures. Among the large group of organic acids and esters are e.g. propionic acid with a boiling point of 141°C up to e.g. palmetic acid with boiling point 351°C, which can also be used as attractive solidifying media in the method of the invention. Preferably the polar organic liquid preferably comprises an alcohol.

In a very attractive embodiment, the solidifying medium comprises glycol, such as ethylene glycol, propylene glycol or a polyethylene glycol or mixtures thereof. Preferably, propylene glycol, ethylene glycol or mixtures thereof are used; most preferably ethylene glycol is used.

Ethylene glycol has an atmospheric boiling point of 197°C, and can be used in any mixture with water. Ethylene glycol is therefore very versatile for use as solidifying medium. Polymers having a high melting point, such as polyester and polycarbonate can be subjected to underwater granulation resulting in small particles of high sphericity and roundness using ethylene glycol, optionally in admixture with water, as solidifying medium.

In a preferred embodiment, the heat conductivity of the solidifying medium is below 0.55 W/m/°C (or W/m/K), preferably below 0.50 W/m/°C, more preferably below 0.40 W/m/°C, most preferably below 0.30 W/m/°C. The heat conductivity of ethylene glycol is 0.26 W/m/°C, whereas that of water is 0.609 W/m/°C. It may even be preferred to have an even lower heat conductivity as low as below 0.20 W/m/°C. N-butylalcohol has a very low heat
conductivity of 0.167 W/m/°C, and a boiling point of 117.5°C. Heat conductivity is to be measured at atmospheric pressure and at room temperature, i.e. 20°C. The heat conductivity of many liquids are known, and are published e.g. on the website www.toolbox.com. The heat conductivity can be measured according to the ASTM D2717 standard, e.g. with the LabTemp30190 equipment of PSL Systemtechnik (Clausthal-Zellerfeld, Germany) according to the instructions of the manufacturer.

It has been observed that the heat conductivity plays an important role in the avoidance of clogging of the die outlet openings, in particular when polymers having a high melting point of e.g. 300°C or higher are used in the underwater granulation process. A higher heat conductivity would allow to absorb a great amount of heat by the solidifying medium from the melt as it passes the die outlet opening, having the risk that the melt solidifies as it is still at the die outlet opening by direct cooling in contact with the solidifying medium or indirect cooling via the die-plate surface, resulting in clogging of the die outlet opening. A lower heat conductivity of the solidifying medium ensures a slower solidification of the melt in the solidifying medium, avoiding clogging at the die outlet opening. Also, when the particles are solidified slowly, there is more time to allow the particles to adapt to the thermodynamically preferred spherical state, therewith improving the roundness and sphericity of the particles.

Another embodiment of the invention comprises the use of flow-aids during extrusion and/or solidification of the particles in order to facilitate the formation of small spherical and round particles. These flow-aids can be any known melt viscosity reducing agent such as wax, liquid or solid flame retardant, organic solvent, hydrocarbons in general etc. It is obvious to those skilled in the art that these flow aids may have a negative effect on the compressive strength of the particles. In another preferred embodiment of the present invention these flow-aids are removed from the particles once they are solidified in whole or in part in a subsequent process step by known extraction agents such as water, organic alcohols such as glycols or any appropriate extraction medium.

In order to produce particles of the required small size, the outlet opening of the die preferably has a diameter of below 1.0 mm, more preferably below 0.8 mm, even more preferably below 0.75 mm. The outlet opening of the die is preferably above 0.3 mm, preferably above 0.4 mm.

In a particular embodiment of the invention the outlet opening of the die cooperates with a cutting device, cutting the melt passing through the die. By cutting the melt, portions of the melt are individually solidified. In the art methods are known for cutting the melt that exits a die. For example cutter blades circling around the die outlet opening are known for this purpose. Straight and angled cutter blades can be used and spacing between the cutter blades is critical to the process. Because of the surface tension of the melt, the melt rounds
up upon solidification in the solidifying medium. The melt is preferably passed through the
die at a flow rate and wherein the cutting device is synchronized with the said flow rate such
as to cut off equal portions of the passed melt. By synchronizing the cutting frequency with
the flow rate of the melt through the die outlet opening, it is possible to cut the melt at a
predetermined length therewith controlling the shape of the particles to be formed upon
solidification.

Preferably the portions of the melt after passing through the die and being cut by the
cutting device have a length that corresponds with 0.7 to 5 times, in particular to 3 times,
more in particular to 1.3 times the diameter of the outlet opening of the die. More preferably,
said length corresponds with the said diameter, in order to produce spherical particles.

The particles preferably have a particle size of 1.2 mm or lower, more preferably 1.1 mm or
lower, even more preferably 1.0 mm or lower, still more preferably of 0.9 mm or lower, most
preferably 0.8 mm or lower. The particles preferably have a particle size 0.3 mm or more,
more preferably 0.4 mm or more. Said particle sizes can be conveniently obtained by the
choice of the diameter of the die outlet opening and of the length of the cut melt as indicated
above.

Many polyester and polycarbonates are known that are suitable to be used as polymer
for the polymer comprising particle of the present invention. In particular, the polyester in the
melt preferably comprises a cross-linked polymer, a cross-linked copolymer, a cross-linked
terpolymer, a cross-linked block(co) polymer or a mixture thereof. This crosslinking improves
the strength of the particles at higher temperatures, and decreases the so-called creep
behaviour (the tendency to liquefy).

During the production process, the polymer is thermoplastic. The thermoplastic nature
is also of advantage for proppant particles in order to minimize abrasion in the fractures,
which is e.g. explained in US7,322,411, herein incorporated by reference.

The polymer is preferably comprises a polyester, one or more aromatic or aliphatic
partially crystallized polyesters. The said polymers preferably have a softening point, melt
temperature and compressive strength as described above in order to be usable as a
proppant.

As indicated above, the polymer preferably comprises a thermoplastic polymer.
Examples of suitable thermoplastic polymers include aromatic polyesters and aliphatic
polyesters, liquid crystalline polyesters, polycarbonates.

As densities of a typical fracturing fluid are often about 1.1 to 1.5 g/ml, the polymer
may include reinforcing materials and still be a suitable as proppant.

Polyamides may be homopolymers, copolymers, terpolymers, or higher order
polymers. Blends of two or more polyamides may be used.

The polymer preferably comprises polyethylene terephthalate (PET), preferably cross-
linked, the polyethylene terephthalate preferably being recycled polyethylene terephthalate, most preferably cross-linked recycled polyethylene terephthalate. Polyethylene terephthalate, in particular cross-linked polyethylene terephthalate has appeared to be a very suitable polymer to be used as proppant, i.e. having the desired properties as discussed above. In a very attractive embodiment the polyethylene terephthalate is recycled polyethylene terephthalate, preferably cross-linked.

In another attractive embodiment, the polymer comprises polycarbonate.

Preferably the polymer melt comprises a filler. The filler can be used to reinforce the particles, and also to modulate the specific weight of the particles and reduce cost. The filler should be capable of reinforcing the polymer, while also reducing the potential for crush as exemplified below.

The filler is preferably chosen from the group of a filler polymer, sand, carbon black, graphite, mica, silica, silicon carbide, alumina, quartz, nanotubes, coconut, walnut, natural fibre, glass fibre, glass beads, hollow glass spheres, glass powder, glass fibres, ceramics, grits, clays (e.g., kaolin), staurolite (including staurolite sand) and wollastonite or a combination thereof. The fillers may be in a variety of forms such as ground particles, flakes, needle-like particles and the like. The size and form of the particles should be selected such that they may easily be incorporated into the polymeric carrier and allow for the formation of proppants having the desired size. The filler polymer can be another polymer or a mixture of polymers, other than the polyester and or polycarbonates as described above. The filler polymers can e.g. contribute to the material density. E.g PET has a material density of 1.4 g/cm³. In order to provide a melt of a lesser material density, a filler polymer can by admixed, that has a lower material density, such as e.g. polyethylene, having a material density of 0.9 g/cm³. The ratio of the polyester/polycarbonate in the melt to the filler polymer is preferably chosen such, that the material density of the melt in solidified state is 1.1 - 1.5 g/cm³, preferably 1.2 - 1.3 g/cm³.

The fillers preferably have a Mohs hardness of at least about 3, or more preferably of at least about 5, or yet more preferably of at least about 6, or still more preferably of at least about 7.

The fillers may optionally be pre-treated with one or more compatibilising and/or coupling agents that facilitate adhesion to or other compatibility with the polymer. Compatibilising and/or coupling agents may also be added to the filler and polymer mixture prior to or during melt blending to form the proppants. The compatibilising and/or coupling agents may be used in about 0.01 to about 1 weight percent when they are added prior to or during melt blending. Examples of coupling agents suitable for use with sand or glass are silane coupling agents such as gamma-aminopropyltriethoxysilane (silane A-1 100).
Preferably the particles according to the invention comprise about 20 to about 100 weight percent of polymer and about 80 to about 0 weight percent filler and/or other additives, wherein the weight percentages are based on the total weight of the particles. In a particular embodiment of the invention the polymer comprises 100% polymer. In another embodiment the particles according to the invention comprise about 20 to about 80 weight percent of polymer and about 80 to about 20 weight percent filler and/or other additives.

The melts for the particles according to the invention that comprise one or more fillers can be formed by melt blending the fillers with the polymers. Any melt blending technique known in the art may be used. For example the component materials may be mixed using a melt-mixer such as a single- or twin-screw extruder, blender, kneader, roller, Banbury mixer, etc.

In a very attractive embodiment the melt is passed through a die plate having a plurality of dies. In this way, many particles can be produced in parallel simultaneously. A suitable die plate is e.g. described in US7,776,244. Therein the die plate is used for the preparation of expandable polystyrene. However particles according to the present invention are preferably not expandable, which means that the material density of the solid particles does not significantly differ from that of the originating melt, and that the melt did not contain blowing agent. Preferably the outlet openings of the dies of the plate are equal, enabling the preparation of particles of equal size. In case a plurality of dies are used, the term 'reduced' with respect of the closure of the die outlet opening by solidification of the melt at the die outlet opening may also relate to the number of die outlet openings that are closed or partially closed as compared to the number of dies (partially) closed under the same process conditions without the above described temperature control.

The die preferably has an inlet having an inlet opening having a diameter being larger than that of the outlet opening. The outlet comprises a number of individual outlet channels having a channel diameter. The outlet channel preferably has an inlet diameter that is at least equal to the outlet diameter. The die further preferably comprises a die area located upstream of the channels having a diameter of at least the diameter of the outlet opening. The channel has preferably a total length of at least two times the diameter of the outlet diameter, preferably 6-4 times. These features are further in detail described in US7,776,224, herein incorporated by reference and it has been found that these features contribute to an equal flow distribution over the number of outlet channels and thereby to a uniform particle diameter.

The pressure upstream of the die outlet opening is up to 250 bar, preferably up to 200 bar, more preferably up to 150 bar. The pressure is preferably at least 60 bar, more preferably at least 90 bar. As described above, the pressure may be of influence to the clogging of the outlet opening of the die. A higher pressure may give less clogging.
Attractively, the particles are recovered from the solidifying medium. Many state of the art methods can be used to recover the particles, e.g. by filtration, centrifugation or by treatment in a cyclone.

In another embodiment the particles can be dried and sieved. Preferably, the particles are dried after recovery, i.e. by exposure to a stream of air or an inert gas. In case water was used as solidifying medium, the particles are preferably dried by air. In case an organic liquid was used as solidifying medium it can be contemplated to wash the recovered particles with water or any other liquid first. However the recovered particles can also be dried without being washed. In that case, an air stream can be used to dry the particles. It can also be advantageous to use an inert gas such as nitrogen for drying. By washing with water, the temperature of the particles may drop to an undesirably low temperature. The temperature is preferably kept as high as possible in order to provide for a cost effective drying process. Said drying can e.g. take place in a vertical falling bed, wherein the particles flow downward, and wherein the drying medium such as air or nitrogen is blown in counter current upward direction. The crystallisation and drying step can preferably be efficiently combined into one unit operation.

If desired, e.g. when PET is used for the preparation of the proppant particles, the particles can attractively be cured by incubation of the particles at or above the crystallisation temperature $T_{pc}$ thereof. Such a curing step, or crystallisation step, provides additional hardness to the particles. This curing or crystallisation can e.g. take place in a residence time crystalliser.

The crystallisation temperature is explained in figure 1 below. Although a separate curing step can be performed, the said curing can attractively take place during the solidifying process in the solidifying medium. In that case, the temperature of the solidifying medium must be chosen to be above the said $T_{pc}$ of the particles. The curing step can also attractively be combined with the drying step. In that case, the temperature of the drying medium should be above the said $T_{pc}$ of the particles. Or the curing step can be performed by use of the latent heat of the particles or by external heating or by a combination thereof.

The invention also relates to a particle, obtainable by the method according to the invention, having a particle size of 1.3 mm or less, preferably of 1.0 or less, more preferably of 0.8 or less, most preferably of 0.7 mm or less. It is to be understood that when a particle, that can be regarded as round and spherical, has a particle size of e.g. 1.0 mm, said particle will pass through a 1 mm sieve, whereas it will not pass a sieve of a smaller mesh size. This way, particle sizes can be easily controlled.

The particles according to the invention preferably have a material density of 1.0 - 2.1 g/ml (or g/cm$^3$). The particles preferably have a density of above 1.05. Also, the particles preferably have a density of below 1.8 g/ml, preferably below 1.35 g/ml and most preferably
below 1.10 g/ml. To this end, the composition of the particle, comprising the polymer(s) and optionally filler(s) are preferably chosen to correspond with the said density.

As described above the particles should preferably stay in suspension during the fracturing process. This is achieved by modulating the material density to close to that of the fracturing fluid.

Preferably, the particles obtainable by the method according to the invention have a particle size of 0.3 - 1.3 mm, more preferably of 0.3 - 0.9 mm, most preferably of 0.4 - 0.8 mm. These sizes can be conveniently be obtained by choosing a diameter of the die outlet opening to be equal to or somewhat smaller or larger than the envisaged particle size, and to synchronize the cutting device with the flow rate of the melt passing the die outlet opening accordingly, preferably to allow a length of the cut melt to be 0.7 to 1.3 times the said diameter. By solidification, the cut melt solidifies into a spherical particle of optimal roundness and sphericity. There is a great demand for such particles, in particular for use as proppants. It is to be observed that the particles, produced according to the method of the present invention are not significantly larger than the diameter of the corresponding die holes, which is in contrast with the use of polyamides, where significantly larger particles are produced than the diameter of the corresponding die holes.

Both the polymer and filler(s) that are part of the particles of the invention should be relatively stable in the presence of typical down hole chemical environments and at the temperatures and pressures encountered in the application. For example, polyester resins are well known for their stability as engineering polymers under a variety of conditions. The stability requirements for a particular well depend e.g. on the temperature, pH, and pressure present and exposure time to these conditions that is required. To this end, the polymer comprising particle according to the invention preferably has an acid solubility according to the API19C-8 standard of less than 5 %. Further, the polymer comprising particle preferably has a compressive strength of at least 45 N/mm², preferably at least 50 N/mm², more preferably 70 N/mm², most preferably 100 N/mm² as measured as indicated above and in the examples.

The compressive strength is preferably measure at a higher temperature. The higher the temperature, the more the polymer tends to soften and to be less resistant to pressure. So polymers that have the required compressive strength at higher temperatures can be used at higher temperatures as well. Such temperatures are 80°C, 100°C, or 150°C or the operating temperature.

In a further preferred embodiment the particles according to the invention has a roundness and/or a sphericity of 0.7 - 1, preferably of 0.8 - 1 and even more preferably of 0.9 - 1 according API19C. Such roundness can be obtained by underwater granulation techniques. Crushing elongated polymer bars into smaller particulate may also be an option,
however this involves an additional processing step.

The particles according to the invention preferably have a pellet weight of 0.6 g or less. The term pellet weight is the weight of exactly 100 particles, and is therewith a convenient indication of the particle size.

The invention further relates to a collection of particles comprising a combination of a first plurality of particles according to the invention having a first diameter, combined with a second plurality of particles according to the invention having a second diameter, the second diameter being different from the first diameter. By this a mixture of particles of different size is provided. The first plurality of particles can e.g. be produced with a first die, having another diameters for the die outlet opening as a second die, used for the preparation of the second plurality of particles.

In a very attractive embodiment of the invention, the particles according to the invention or as defined by the method of the present invention are proppant particles. However the particles can be used for any desired purpose.

In another embodiment the polymer comprising particles according to the invention are used as component in a fracturing fluid.

The invention also relates to a fracturing fluid comprising particles according to the invention.

The invention also relates to a process for hydraulic fracturing of subterranean formations, comprising introducing a fluid in which particles according to the invention or as prepared according to the method according to the invention are suspended into an oil or gas well surrounded by rock, such, that fractures are created in the rock and some or all of the polymer comprising particles flow into the fractures.

Attractively, in the above process, particles of a first particle size are suspended in a first fluid and introduced into the oil or gas well in a first step, followed by at least a subsequent second step, wherein particles of a second particle size are suspended in a second fluid and introduced into the oil or gas well, wherein the second particle size is larger than the first. By this two-step approach, smaller particles are allowed to enter the smaller regions of the fractures, where after larger particles are provided to be positioned in wider regions of the fractures.

Accordingly, the first step can preferably be followed by a plurality of subsequent steps, wherein each subsequent step differs from the preceding step in that the particle size of the subsequent step is larger than of the preceding step. This way, increasingly larger particles are provided in subsequent steps.

The invention will now be further explained by the following figures and examples, wherein:
Figure 1 is a graph, showing a DSC curve according to ISO 11357-1 1997.

Figure 2A-1 show pellets of several samples as prepared according to the invention.

Figure 3 shows a reference table taken from the standard API19C for the determination of particle roundness and sphericity.

Figure 4 is a schematic diagram of an apparatus for determination of the compressive strength of the particles of the invention, and

Figure 5 is a printout including a graph and a table, generated by software of the compressive strength measuring apparatus.

Referring to figure 1, which is taken from ISO 11357-1 1997, to which is expressly referred to herein, polymers may display specific behaviours called "glass transition", "crystallisation" and "melting" as shown in the figure by 'g', 'c' and 'm', respectively. These transitions are characterised by the energy required for these transitions and thereby become measurable as described in IS01 1357. Of relevance is T, the peak indicating the melting point of the polymer, although polymers have a melting range starting at T and ending at T,T, and T,T, can easily be determined following the instructions of the ISO 11357 protocol.

In figures 2A-I pellets of samples RPI139, RPI147, RPI085, RPI114, RPI071, RPI103, RPI056, RPI183 and RPI196 are shown respectively. Particles are encircled that we used to assess roundness and sphericity according to standard API19C, see also the below examples. Each figure 2A-I also shows a reference table that is magnified in figure 3.

Figure 3 shows a reference table, used in standard API19C to determine the roundness and sphericity.

Figure 4 is a schematic graph of the apparatus Instron 3366 as used in the examples to determine the compressive strength of the particles of the invention. In a heating chamber C, a lower static plate A of a larger diameter and an upper moving plate B of a smaller diameter B, oriented in parallel to plate A, are accommodated. A particle D is placed on static plate A. During operation, plate B moves downward towards static plate A, therewith exerting pressure to the particle D resulting in deformation of the particle. Both pressure and distance between plates A and B are recorded by the apparatus.

Figure 5 shows a print out generated by Bluehill software of the Instron apparatus of figure 4. In the graph, at the X-axis, the compression is indicated in mm, whereas on the Y-axis the compression force is given in Newton (N). The diameter of the uncompressed particle can be read from the table generated by the Bluehill software. The compressive strength of 15 samples was tested, samples 1 - 5 were tested at 80°C, and samples 6 - 15 at 100°C. The size of the particles was determined by measuring the diameter of the uncompressed particle by measuring the distance between plates A and B at the moment
that resistance is measured. The force needed to effect 0.1 mm compression is given in the second column of the upper table, and the force needed to effect 0.2 mm compression is given in the second column of the upper table. These data are also presented in the graph.

5 Examples

EXAMPLE 1

Preparation of pellets

10 Starting materials

Polymers
Poly carbonate (PC18) : Xantar 18 UR, Mitsubishi Engineering-Plastics Corporation 40549 Dusseldorf, Germany.
Poly ethyleneterephthalate (PET): polyclear 1101, Invista B.Bigles CH-6301 Zug, Switzerland.
Recycled poly ethyleneterephthalate (rPET): CorePET FR80 grün, Pet Recycling, Arnhem, Netherlands.

Fillers
Calcium carbonate: EXH1-OM, Omya D-89537 Giengen-Burgberg, Germany.
Wollastonite 95, S&B Industrial Minerals GmbH, Otavi Minerals, D-41460 Neuss, Germany

20 Ethylene glycol
Mono Ethylen Glycol (MEG) Art. Nr. 93.50.2682, Wittig Umweltchemie GmbH, Grafschaft bei Bad Neuenahr-Ahrw, Germany

A polymer melt of starting materials according the formulations as given in table 1 was added via standard loss-in-weight feeders to the throat of a 6 barrel long extruder (Berstorff ZE60, Germany) a twin screw length of 2400 mm equipped with a standard vacuum set-up. At the outlet of the extruder, a screen pack changer with 630/315 sieve (K-SWE-121/RS, BKG, Germany) was installed to free the polymer melt from any solid particles followed by a 70/70 high pressure melt pump (BKG, Germany) to generate the required die plate pressure, as given in table 1. The polymer melt was passed through a multiple die-plate with a die-opening arrangement according to figure 2, the outlet opening having a
a diameter of 0.5 and 0.75 mm, respectively, as shown in the table below and cut to size by a cutter hub on a pelletizer (type AH2000, BKG, Germany). The solidifying medium was water or ethylene glycol having a temperature as indicated in table 1. The process parameters for each formulation can be found in table 1.

5 Determination of the theoretical particle size

From the extruder throughput, the density of the material, the number of die outlet openings, the cutting frequency of the cutter hub (to be determined by the number of blades on the cutter hub and the speed of the cutter hub) one skilled in the art can easily calculate the expected particle size. In the example of RPI139, the throughput was 300 kg/h, the number of die outlet openings was 450 and the melt passing each die outlet opening was cut by 10 knives, rotating at 3515 rpm (rotations per minute). The density of the material was 1340 kg/m³. The volume of the pellets can be calculated by the formula throughput per second per die outlet opening divided by the density of the polymer melt, divided by the cutting frequency of the cutter hub per second. In this example, the particle volume is therefore 300/3600/450/1 340/1/(351 5/60)*10⁻⁹=0.236 mm³. This makes an expected particle size of about 0.76 mm diameter, as the shape is assumed to be spherical (volume = πr/6*d³, i.e. 3.14/6*0.76³=0.236 mm³).

20 Determination of the actual particle size.

The above expected particle size was compared with the actual particle size. The latter was obtained by weighing 100 particles (herein also 'pellets') on a Sartorius A200S micro-scale from Sartorius GmbH, Gottingen Germany. From the said weight, one skilled in the art can now calculate the actual average pellet volume and size through the known density from the formulation. An actual pellet weight above the theoretical particle weight is an indication of die-holes being clogged, as the same volume of material is passing through a lower number of open die outlet openings, resulting in a proportionally higher volume per open die outlet opening. In this example the weight of 100 pellets is 0.0395 gram, or a volume per pellet of 0.0395*10/1.34=0.295 mm³ so the number of open holes is 450 *0.236/0.295=360. The acceptable limit for weight of 100 pellets can be calculated upfront from the maximum allowable pellet size that is specified. Production was halted approaching this limit to free the frozen die-holes.

Individual particle size was also measured by measuring the diameter of individual pellets as outlined above and further explained below when determination of compressive strength is discussed.
Separation of the pellets

The water/pellet slurry was separated in a standard centrifugal dryer. The remaining solidifying medium that passes through the centrifugal dryer 0.3 mm sieve was treated in a BKG Optigon filter drum (BKG, Germany) to remove the undersized pellets and to recuperate the solidifying medium that was recycled back to the pelletizer. The undersize pellets were either wasted, or remelted and recycled into the extruder. The hot and dried pellets coming of the centrifugal dryer were subsequently sieved on a 1.0 mm sieve to remove oversized material before packaging. The oversized material was wasted, or remelted and recycled into the extruder. In case of RPI139 and RPI183, the final product was then crystallised in an infra-red rotary drum crystalliser at 175°C and a residence time of 17 minutes.

Determination of pellet roundness and sphericity

10 individual pellets of different samples as enclosed in figures 4A-I were visually examined for roundness and sphericity and valued in accordance with the standard API19C, of which a relevant reference table is shown in figure 4. For sample for RPI139, the average sphericity was e.g. determined to be 0.8 and the average roundness to be 0.9, based on the data as presented in the table of figure 3A. These averages are also presented in the above table 1.

Calculation of the pellet density (specific gravity).

The specific gravity was calculated from the specific gravity of the individual components in the actual ratio of the formulation. In case of example RPI139 the specific gravity was equal to the single component PET being 1.34 g/ml.

In case of example RPI085 the formulation consists of 85 wt.% polyethylene terephthalate with a specific gravity 1.34 g/ml and 15 % wollastonite with a specific gravity of 2.70 g/ml. The composition therefore has a specific gravity of 0.85*1.34+0.15*2.70=1.61 g/ml.
Table 1: Starting materials and production parameters

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Sample</th>
<th>RPI065</th>
<th>RPI114</th>
<th>RPI119</th>
<th>RPI147</th>
<th>RPI139</th>
<th>RPI143</th>
<th>RPI193</th>
<th>RPI196</th>
<th>RPI111</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extruder temperature</td>
<td>°C</td>
<td>265</td>
<td>320</td>
<td>290</td>
<td>285</td>
<td>270</td>
<td>280</td>
<td>310</td>
<td>320</td>
<td></td>
</tr>
<tr>
<td>Extruder RPM</td>
<td>250</td>
<td>199</td>
<td>349</td>
<td>350</td>
<td>219</td>
<td>350</td>
<td>350</td>
<td>200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Die plate type</td>
<td>Nr. of holes</td>
<td>450</td>
<td>360</td>
<td>450</td>
<td>450</td>
<td>380</td>
<td>450</td>
<td>360</td>
<td>360</td>
<td></td>
</tr>
<tr>
<td>(holes in mm²)</td>
<td>0.5</td>
<td>0.75</td>
<td>0.5</td>
<td>0.75</td>
<td>0.5</td>
<td>0.75</td>
<td>0.75</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature of the melt °C</td>
<td>301</td>
<td>324</td>
<td>338</td>
<td>336</td>
<td>317</td>
<td>337</td>
<td>385</td>
<td>320</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Feed rate Kg/h</td>
<td>300</td>
<td>300</td>
<td>300</td>
<td>300</td>
<td>300</td>
<td>300</td>
<td>300</td>
<td>300</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Die plate pressure MPa</td>
<td>23</td>
<td>15</td>
<td>23</td>
<td>23</td>
<td>24</td>
<td>18</td>
<td>22</td>
<td>25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cutter hub Nr. Of knives</td>
<td>12</td>
<td>12</td>
<td>16</td>
<td>12</td>
<td>16</td>
<td>18</td>
<td>18</td>
<td>18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pelletizer speed RPM</td>
<td>3629</td>
<td>3620</td>
<td>3515</td>
<td>3534</td>
<td>3678</td>
<td>3619</td>
<td>3656</td>
<td>3620</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solidifying medium flow m³/h</td>
<td>30</td>
<td>31</td>
<td>29</td>
<td>29</td>
<td>31</td>
<td>14</td>
<td>20</td>
<td>31</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solidifying medium temperature °C</td>
<td>95</td>
<td>84</td>
<td>94</td>
<td>92</td>
<td>85</td>
<td>115**</td>
<td>121**</td>
<td>91</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pellet weight per 100 Gram</td>
<td>0.0424</td>
<td>0.0539</td>
<td>0.0395</td>
<td>0.0439</td>
<td>0.0458</td>
<td>0.0193</td>
<td>0.0230</td>
<td>0.0337</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pellet size mm</td>
<td>0.79</td>
<td>0.79</td>
<td>0.83</td>
<td>0.80</td>
<td>0.76</td>
<td>0.65</td>
<td>0.72</td>
<td>0.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sphericity</td>
<td>0.7</td>
<td>0.7</td>
<td>0.8</td>
<td>0.7</td>
<td>0.8</td>
<td>0.9</td>
<td>0.9</td>
<td>0.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Roundness</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>1200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Specific gravity Kg/m³</td>
<td>1610</td>
<td>2050</td>
<td>1340</td>
<td>1610</td>
<td>1880</td>
<td>1340</td>
<td>1200</td>
<td>227</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Compressive strength at 80°C N/mm²</td>
<td>62</td>
<td>55</td>
<td>58</td>
<td>66</td>
<td>71</td>
<td>64</td>
<td>66</td>
<td>0.61</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Measured at 20°C.

** Solidified in ethylene glycol.
Determination of the compressive strength

The compressive strength was determined for individual particles at 20% uniaxial compression at an elevated temperature of 80°C. Uniaxial means that compression takes place in a single axis, e.g. by moving the two parallel oriented plates towards each other.

For this measurement, a compression tester from Instron type 3366 was used, see also figure 5. This instrument comprises a dual column load frame with a 10000N load cell. This load frame is usually used in polymer testing of tensile bars and has internal equipment needed for tensile bars, but in this application the apparatus is used in compressive mode.

The apparatus was controlled using Bluehill software version 2.29. The operation of this frame is fully described in the operator guide M10-16281-EN Revision B and system support M10-16282-EN Revision A. Between the dual columns a heated oven Instron model 3119 was installed wherein the load cell and the 2 plates were accommodated to be able to uniformly heat the sample during testing and to perform the test at a required temperature. In this example, the temperature is set at 80°C, although another temperature such as 100°C can also be set.

Individual pellets are placed between 2 flat plates. The load cell measures the force to compress an individual polymeric particle of the relevant size. The load measurement is digitally recorded as a function of the compression. To calibrate the compression tester it is a standard requirement to run a compression test without a particle to measure the deformation of the equipment used and all measurements must be corrected accordingly. This compensation is a feature of the Bluehill software.

The compression test is fully automatic and measures the load and the compression simultaneously. The upper plate of the load cell is moved towards the lower plate, on which the particle to be tested is placed. As soon as the upper plate arrives at the particle, a pressure resistance is recorded by the apparatus. The onset of the measurement is taken when a load of 1 N is detected on the load cell, and the diameter of the individual pellet is recorded at this point, based on the distance between both plates. Upon increasing the load, the load versus compression is digitally recorded by the Bluehill software, and a graph of the progressing test is generated, see figure 5 for a particle of sample RPI139. As an example specimen 1 will be used.

The pressure at the point of 20% compression is now to be calculated. In the graph of figure 6, the particle size was determined by the apparatus to be 0.53 mm. This means that 20% compression is 0.106 mm. From the table, it can be seen that 0.106 mm corresponds to a compressive force of slightly above 9.49 N. The exact value can however be taken from a digital table that the Bluehill software generates (not shown). The compressive strength is the load divided by the contact surface. The contact surface is
calculated by dividing the volume of the original pellet by the compressed height (For calculation reasons, the shape of the particle is assumed to be cylindrical, therewith neglecting the fact that the actual contact surface will be somewhat lower than the assumed surface because upon compression, a spherical particle will take the form of a barrel rather than of a cylinder). In this case the volume of the original pellets is \(3.14/6 \times 0.53^2 = 0.0779\) mm\(^3\). The contact surface at 20% compression now is \(0.0779/(0.53 \times 0.8) = 0.184\) mm\(^2\). The compressive strength is therefore \(9.49/0.184 = 51.6\) N/mm\(^2\).

**EXAMPLE 2**

Samples of RPI183 and RPI196 were produced by using ethylene glycol as solidifying medium at a temperature of 115°C and 121°C respectively. This solidifying medium has a lower heat conductivity than water (water: 0.6 W/m°C whereas most organic liquids have a substantially lower heat conductivity in the range of 0.1-0.2 W/m°C). Therefore the relatively cold solidifying medium flowing along the die-plate is causing a reduced temperature loss of the melt at the die outlet openings of the die plate. Organic fluids, in particular liquids having a boiling temperature of more than 100°C, preferably between 100 - 200°C are suitable as solidifying medium, as long as said fluids do not significantly react with the polymeric melt passing through the die outlet opening. Preferably, the solidifying medium is inert with respect of the said polymeric melt. The skilled person is capable to choose a suitable fluid, and to adapt the equipment if necessary, i.e. by adapting the chamber wherein the solidifying medium is accommodated. This enables the production of smaller pellets using common pelletizing equipment. From the table it can e.g be observed that high values are obtained for roundness and sphericity of the particles of the samples RPI183 and RPI196.
CLAIMS

1. Method for the preparation of particles having a particle size of 1.3 mm or less, the particles comprising at least a polymer chosen from the group consisting of a polyester, a polycarbonate or a mixture thereof, wherein a melt comprising the said polymer has a density of 1.0 to 2.1 g/ml in solidified state, and is extruded by passing the melt through at least a die with a diameter of at most 1.2 mm into a solidifying medium having a temperature of below the melting temperature \( T_{pm} \) of the melt, allowing the melt to solidify in the solidifying medium into the particles, the temperature of the melt at the die outlet opening being controlled such, that closure of the die outlet opening by solidification of the melt at the die outlet opening is reduced.

2. Method according to claim 1, wherein said controlling of the temperature of the melt at the die outlet opening comprises holding the temperature of the said die, at least at the outlet opening thereof, at a temperature higher than 60°C below the melting temperature \( T_{pm} \) of the polymer.

3. Method according to claim 1 or 2, wherein the melting temperature \( T_{pm} \) of the polymer is at least 120°C, preferably at least 150°C, more preferably at least 180°C, most preferably at least 200°C.

4. Method according to any of the preceding claims, wherein the polymer has a VICAT softening point of at least 50°C, preferably at least 70°C.

5. Method according to any of the preceding claims, wherein in step a) the temperature of the melt is at least 180°C, preferably at least 200°C, more preferably at least 230°C, most preferably at least 260°C.

6. Method according to any of the preceding claims, wherein in step a) the temperature of the melt is at least 20°C above the melting temperature \( T_{pm} \) of the polymer, preferably 30°C above the melting temperature \( T_{pm} \) of the polymer, more preferably 40°C above the melting temperature \( T_{pm} \) of the polymer.

7. Method according to any of the preceding claims, wherein the temperature of the solidifying medium is at 50°C or more lower than the melting point of the polymer, preferably 60°C or more lower than the melting point of the polymer, and/or 100°C or less lower,
preferably 80°C or less lower than the melting point of the polymer.

8. Method according to any of the preceding claims, wherein the temperature at the outlet opening of the die is held at a temperature higher than 40°C below the melting temperature $T_{pm}$ of the polymer, preferably higher than 20°C below the said melting temperature $T_{pm}$, more preferably at the said melting temperature $T_{pm}$; even more preferably at least 20°C, still even more preferably at least 30°C above the melting temperature $T_{pm}$ of the polymer.

9. Method according to any of the preceding claims, wherein the temperature at the outlet opening of the die is held at above the melting onset temperature $T_{on}$ of the polymer.

10. Method according to any of the preceding claims, wherein the temperature of the die, at least at the outlet opening thereof, is held by transferring external heat to the die, or by generating heat in the die.

11. Method according to any of the preceding claims, wherein the temperature of the die, at least at the outlet opening thereof is held by transferring external heat to the die by arrangement of at least a channel in the die, located in the vicinity of the die outlet opening and transporting of a heat exchange medium through the said channel; by heat induction of the die at the location of the outlet opening; or by the temperature of the solidifying medium, or a combination thereof.

12. Method according to any of the preceding claims, wherein the temperature of the solidifying medium is above 50°C, preferably above 90°C, more preferably above 120°C, even more preferably above 140°C.

13. Method according to any of the preceding claims, wherein the temperature of the solidifying medium is below 250°C, preferably below 200°C.

14. Method according to any of the preceding claims, wherein the atmospheric boiling point of the solidifying medium is above 90°C, preferably above 100°C, even more preferably above 110°C, still more preferably above 120°C, most preferably above 150°C.

15. Method according to any of the preceding claims, wherein the solidifying medium is chosen from the group consisting of water, liquid salt, or an organic liquid or any mixture
thereof.

16. Method according to any of the preceding claims, wherein the solidifying medium is inert to the melt and the particles.

17. Method according to any of the preceding claims, wherein the solidifying medium comprises an organic liquid, having an atmospheric boiling point of above 90°C, more preferably above 100°C, even more preferably above 110°C, still more preferably above 120°C, most preferably above 150°C.

18. Method according to any of the preceding claims, wherein the solidifying medium comprises a polar organic liquid.

19. Method according to any of the preceding claims, wherein the solidifying medium comprises an alcohol, ether, acid or ester, preferably an alcohol.

20. Method according to any of the preceding claims, wherein the solidifying medium comprises glycol, preferably ethylene glycol or propylene glycol or mixtures thereof.

21. Method according to any of the preceding claims, wherein the heat conductivity of the solidifying medium is below 0.55 W/m°C, preferably below 0.50 W/m°C, more preferably below 0.40 W/m°C, most preferably below 0.30 W/m°C or below 0.2 W/m°C.

22. Method according to any of the preceding claims, wherein the outlet opening of the die has a diameter of below 1.0 mm, preferably below 0.8 mm, more preferably below 0.75 mm and/or above 0.3 mm, preferably above 0.4 mm.

23. Method according to any of the preceding claims, wherein the outlet opening of the die cooperates with a cutting device, cutting the melt passing through the die.

24. Method according to claim 23, wherein the melt is passed through the die at a flow rate and wherein the cutting device is synchronized with the said flow rate such as to cut off equal portions of the passed melt.

25. Method according to claim 24, wherein the portions of the melt after passing through the die and being cut by the cutting device have a length that corresponds with 0.7 to 5 times, preferably to 3 times, more preferably to 1.3 times the diameter of the outlet opening
of the die, most preferably, said length corresponding with the said diameter.

26. Method according to any of the preceding claims, wherein the particles have a particle size of 1.0 mm or lower, preferably of 0.9 mm or lower, more preferably of 0.8 mm or lower, and/or 0.3 mm or more, preferably 0.4 mm or more.

27. Method according to any of the preceding claims, wherein the particles comprise polyester, the polyester in the melt comprising a cross-linked polymer, a cross-linked copolymer, a cross-linked terpolymer, a cross-linked block(co) polymer, or a mixture of two or more thereof.

28. Method according to any of the preceding claims, wherein the polymer is thermoplastic.

29. Method according to any of the preceding claims, wherein the polymer comprises a polyester.

30. Method according to claim 29, wherein the polymer comprises polyethylene terephthalate, preferably cross-linked, the polyethylene terephthalate preferably being recycled polyethylene terephthalate, most preferably cross-linked recycled polyethylene terephthalate.

31. Method according to any of the preceding claims, wherein the melt in solidified state has a compressive strength of at least 45 N/mm² at 80°C.

32. Method according to any of the preceding claims, wherein the polymer melt comprises a filler.

33. Method according to any of the preceding claims, wherein the filler is chosen from the group, consisting of a filler polymer, such as polyethylene, sand, carbon black, graphite, mica, silica, silicon carbide, alumina, quartz, nanotubes, coconut, walnut, natural fibre, glass fibre, glass beads, hollow glass spheres, glass powder, glass fibres, ceramics, grits, clays (e.g., kaolin), staurolite (including staurolite sand), and wollastonite or a combination thereof.

34. Method according to claim 33, wherein the filler polymer has a lower material density than that of the melt, free of the said filler polymer.

35. Method according to claim 34, wherein the filler polymer comprises polyethylene.
36. Method according to any of claims 33-35, wherein the ratio polyester/polycarbonate : filler polymer is chosen such, that the material density of the melt in solidified state is 1.1 - 1.5 g/cm³, preferably 1.2 - 1.3 g/cm³.

37. Method according to any of the preceding claims, wherein in the melt is passed through a die plate having a plurality of dies.

38. Method according to claim 37, wherein the outlet openings of the dies of the plate are equal.

39. Method according to any of the preceding claims, wherein the die has an inlet having an inlet opening having a diameter being larger of that of the outlet opening.

40. Method according to any of the preceding claims, wherein the die comprises a die area located upstream of the outlet opening, having a diameter of at most the diameter of the outlet opening.

41. Method according to claim 40, wherein the die area has a length of at least two times the diameter of the outlet opening, preferably 6-4 times.

42. Method according to any of the preceding claims, wherein the pressure upstream of the die outlet opening is up to 250 bar, preferably up to 200 bar, more preferably up to 150 bar, and/or at least 60 bar, preferably at least 90 bar.

43. Method according to any of the preceding claims, wherein the particles are recovered from the solidifying medium.

44. Method according to claim 43, wherein the recovered particles are dried.

45. Method according to any of the preceding claims, wherein the particles are cured by incubation of the particles at or above the crystallisation temperature T_pc thereof.

46. Method according to any of the preceding claims, wherein the particles are recovered from the solidifying medium and dried.

47. Method according to claim 46, wherein the particles are dried by exposure to a
stream of air or an inert gas.

48. Method according to any of the preceding claims, wherein the particles are cured, preferably during the solidification process or, if performed, during the drying step.

49. Particle, obtainable by the method according to any of the preceding claims, having a particle size of 1.3 mm or less, preferably of 1.0 or less, more preferably of 0.8 or less, most preferably of 0.7 mm or less.

50. Particles comprising at least a polymer, chosen from the group of polyester and polycarbonate, said particles having a density of 1.0 to 2.1 g/ml, a particle size of 1.3 mm or less and a compressive strength of at least 45 N/mm² at 80°C.

51. Particles according to claim 49 or 50, having a density of above 1.05 and/or below 1.8 g/ml, preferably below 1.35 g/ml, most preferably 1.10 - 1.20 g/ml.

52. Particles according to any of the claims 49 - 51, wherein the particles have a compressive strength of at least 45N/mm², preferably of at least 50N/mm², more preferably 100N/mm², most preferably of at least 150 N/mm² at 80°C.

53. Particles according to claim 50, wherein the compressive strength is at 100°C, preferably at 150°C.

54. Particles according to any of the claims 49 - 53, wherein the polymer comprising particles have a particle size of 0.3 - 0.9 mm, preferably 0.4 - 0.8 mm.

55. Particles according to any of claims 49 - 54, having an acid solubility according API19C-8 of less than 5%.

56. Particles according to any of claims 49 -55, having a roundness of 0.7 - 1, preferably of 0.8 - 1, most preferably of 0.9-1.

57. Particles according to any of claims 49 -56, having a sphericity of 0.7 - 1, preferably of 0.8 - 1, most preferably of 0.9-1.

58. Particles according to any of claims 49 - 57, having a pellet weight of 0.6 g or less.
59. A collection of particles comprising a combination of a first plurality of particles according to any of the claims 49 - 58 having a first diameter, combined with a second plurality of particles according to any of claims 49 - 58 having a second diameter, the second diameter being different from the first diameter.

60. Particles according to any of the claims 49 - 59 or as defined in any of the claims 1 - 45, the particles being proppant particles.

61. Use of particles according to any of claims 49 - 60 as component in a fracturing fluid.

62. Fracturing fluid comprising particles according to any of claims 49 - 60.

63. Process for hydraulic fracturing of subterranean formations, comprising introducing a fluid in which particles according to any of claims 49 - 60 or as produced according to a method of any of the claims 1 - 48 are suspended into an oil or gas well surrounded by rock such that fractures are created in the rock and some or all of the polymer comprising particles flow into the fractures.

64. Process for hydraulic fracturing of subterranean formations, according to claim 63, wherein in a first step particles of a first particle size are suspended in a first fluid and introduced into the oil or gas well, followed by at least a subsequent second step, wherein particles of a second particle size are suspended in a second fluid and introduced into the oil or gas well, wherein the second particle size is larger than the first.

65. Process for hydraulic fracturing of subterranean formations, according to claim 64, wherein the first step is followed by a plurality of subsequent steps, wherein each subsequent step, differs from the preceding step in that the particle size of the subsequent step is larger than of the preceding step.
Fig. 1
Fig. 2G

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sphericity</td>
<td>0.9</td>
<td>0.5</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>0.8</td>
<td>0.9</td>
<td>0.9</td>
<td>0.7</td>
<td>0.3</td>
</tr>
<tr>
<td>Roundness</td>
<td>0.5</td>
<td>0.9</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.9</td>
<td>0.7</td>
<td>0.9</td>
<td>0.9</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Fig. 2H

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sphericity</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
</tr>
<tr>
<td>Roundness</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
</tr>
<tr>
<td>Proppant size mm</td>
<td>F @ 0.1 mm (N)</td>
<td>F @ 0.2 mm (N)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------------</td>
<td>----------------</td>
<td>----------------</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>9.49</td>
<td>14.17</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>12.53</td>
<td>17.79</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>12.05</td>
<td>17.66</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>13.55</td>
<td>19.71</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>14.93</td>
<td>21.73</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>9.84</td>
<td>17.30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>9.83</td>
<td>15.71</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>8.99</td>
<td>15.29</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>8.31</td>
<td>14.92</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>8.27</td>
<td>13.68</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>7.25</td>
<td>12.60</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>6.61</td>
<td>10.62</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>8.71</td>
<td>14.12</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>8.35</td>
<td>13.18</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 5
A. CLASSIFICATION OF SUBJECT MATTER
INV. B29B9/06 C09K8/80 E21B43/267

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
E21B C09K B29B

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 practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
</table>

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents:

A: document defining the general state of the art which is not considered to be of particular relevance
E: earlier application or patent or published on or after the international filing date
L: document which may throw doubts on priority claim(s) on which is cited to establish the publication date of another citation or other special reasons (as specified)
O: document referring to an oral disclosure, use, exhibition or other means
P: document published prior to the international filing date but later than the priority date claimed

*T: later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
X: document of particular relevance; the claimed invention cannot be considered without the document being obvious to a person skilled in the art
Y: document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is taken alone
Z: document member of the same patent family

Date of the actual completion of the international search: 2 April 2013
Date of mailing of the international search report: 09/04/2013

Name and mailing address of the ISA:
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016

Authorized officer: Fageot, Philippe
<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Patent document cited in search report</td>
<td>Publication date</td>
<td>Patent family member(s)</td>
</tr>
<tr>
<td>--------------------------------------</td>
<td>------------------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>US 2010285998 Al</td>
<td>11-11-2010</td>
<td>CA 2673086 Al 03-07-2008</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CN 101600549 A 09-12-2009</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EA 200970625 Al 30-12-2009</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EP 2121261 Al 25-11-2009</td>
</tr>
<tr>
<td></td>
<td></td>
<td>FR 2910368 Al 27-06-2008</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TW 200843925 A 16-11-2008</td>
</tr>
<tr>
<td>US 2010285998 Al</td>
<td>11-11-2010</td>
<td>CA 2530966 Al 06-09-2006</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EP 1654103 Al 10-05-2006</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP 4773959 B2 14-09-2011</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP 2007500625 A 18-01-2007</td>
</tr>
<tr>
<td></td>
<td></td>
<td>KR 20060054357 A 22-05-2006</td>
</tr>
<tr>
<td>US 2005035483 Al</td>
<td>17-02-2005</td>
<td>CA 2519144 Al 30-09-2004</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CA 2644213 Al 30-09-2004</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 7210528 Bl 01-05-2007</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 2008032898 Al 07-02-2008</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 2011180260 Al 28-07-2011</td>
</tr>
<tr>
<td></td>
<td></td>
<td>W0 2004083600 Al 30-09-2004</td>
</tr>
</tbody>
</table>