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(54) **METHOD OF TREATING ULTRA-LOW PERMEABLE SUBTERRANEAN FORMATIONS USING PROPPANT PARTICULATES COATED WITH DEGRADABLE MATERIAL**

(71) Applicant: **Halliburton Energy Services, Inc.**, Houston, TX (US)

(72) Inventors: **Feng Liang**, Houston, TX (US); **Bradley L. Todd**, Duncan, OK (US); **Thomas D. Welton**, Houston, TX (US)

(73) Assignee: **Halliburton Energy Services, Inc.**, Houston, TX (US)

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(57) **ABSTRACT**

Methods of treating an ultra-low permeability subterranean formation having a fracture complexity comprising interconnected fractures including providing a fracturing fluid comprising a base fluid and coated proppant, wherein the coated proppant comprise proppant coated with a degradable material; introducing the fracturing fluid into the ultra-low permeability subterranean formation at a rate and pressure above a fracture gradient of the ultra-low permeability subterranean formation; placing the coated proppant into a fracture of the interconnected fractures so as to form a temporarily impermeable proppant pack comprising the coated proppant therein and reduce or prevent the extension of the fracture; reducing the pressure below the fracture gradient; and degrading the degradable material coated onto the coated proppant so as to cause the temporarily impermeable proppant pack to become a permeable proppant pack.

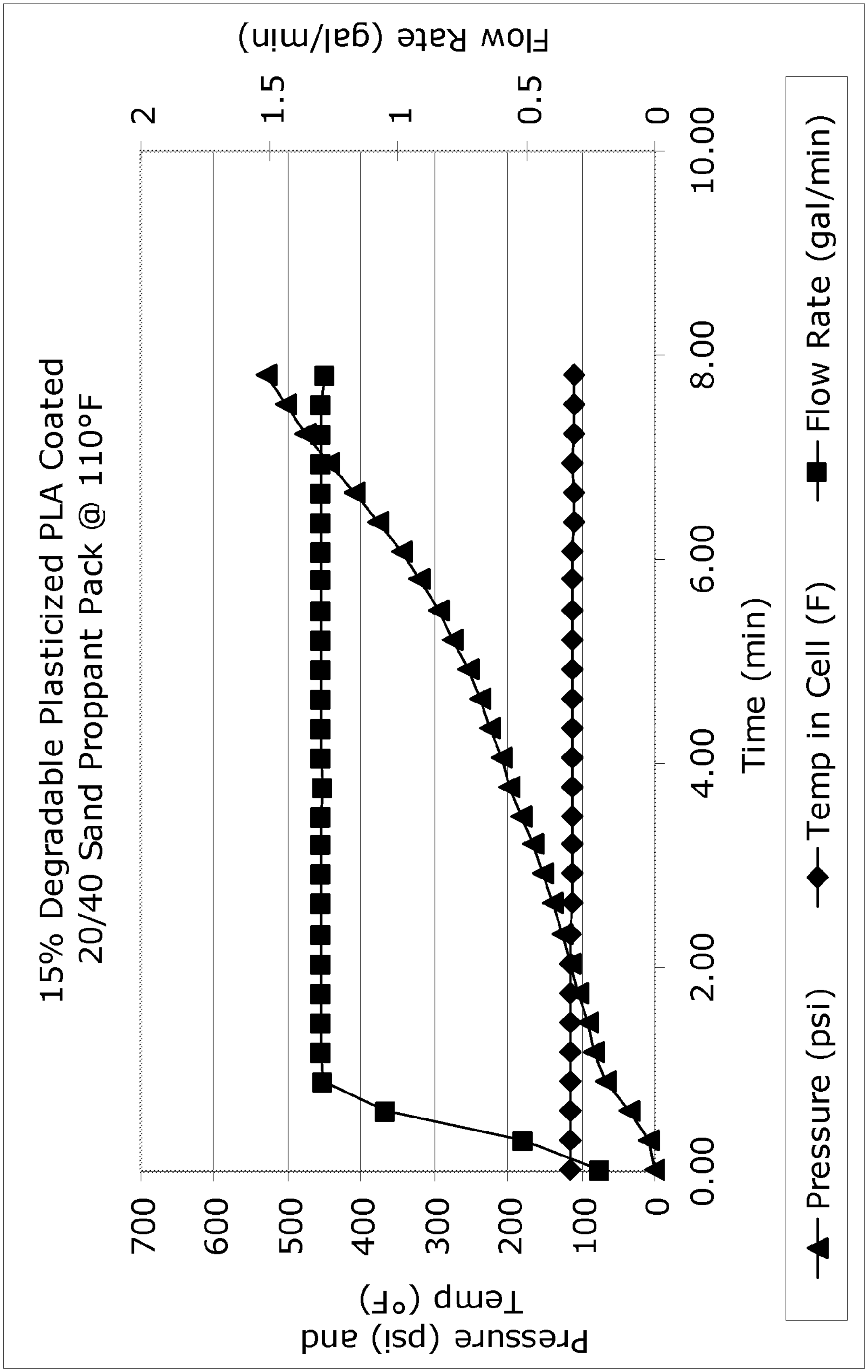
15% Degradable Plasticized PLA Coated
20/40 Sand Proppant Pack @ 110°F
Pressure (psi) and
Temp (°F)
700
600
500
400
300
200
100
0
Flow Rate (gal/min)
2
1.5
1
0.5
0
0.00
2.00
4.00
6.00
8.00
10.00
Time (min)
Pressure (psi)
Temp in Cell (F)
Flow Rate (gal/min)

FIG. 1

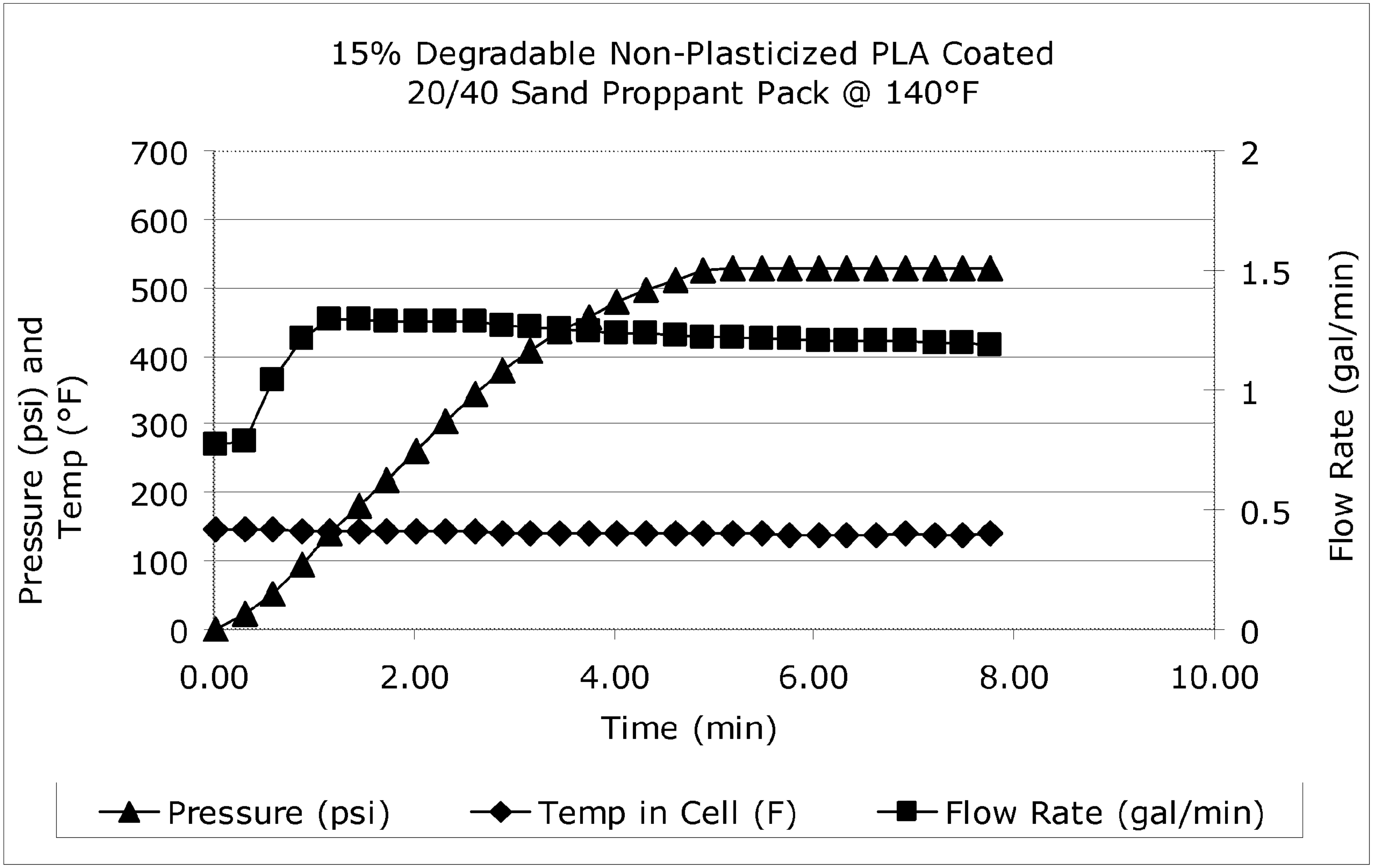
15% Degradable Non-Plasticized PLA Coated
20/40 Sand Proppant Pack @ 140°F
Pressure (psi) and Temp (°F)
700
600
500
400
300
200
100
0
Flow Rate (gal/min)
2
1.5
1
0.5
0
0.00
2.00
4.00
6.00
8.00
10.00
Time (min)
Pressure (psi)
Temp in Cell (F)
Flow Rate (gal/min)

FIG. 2

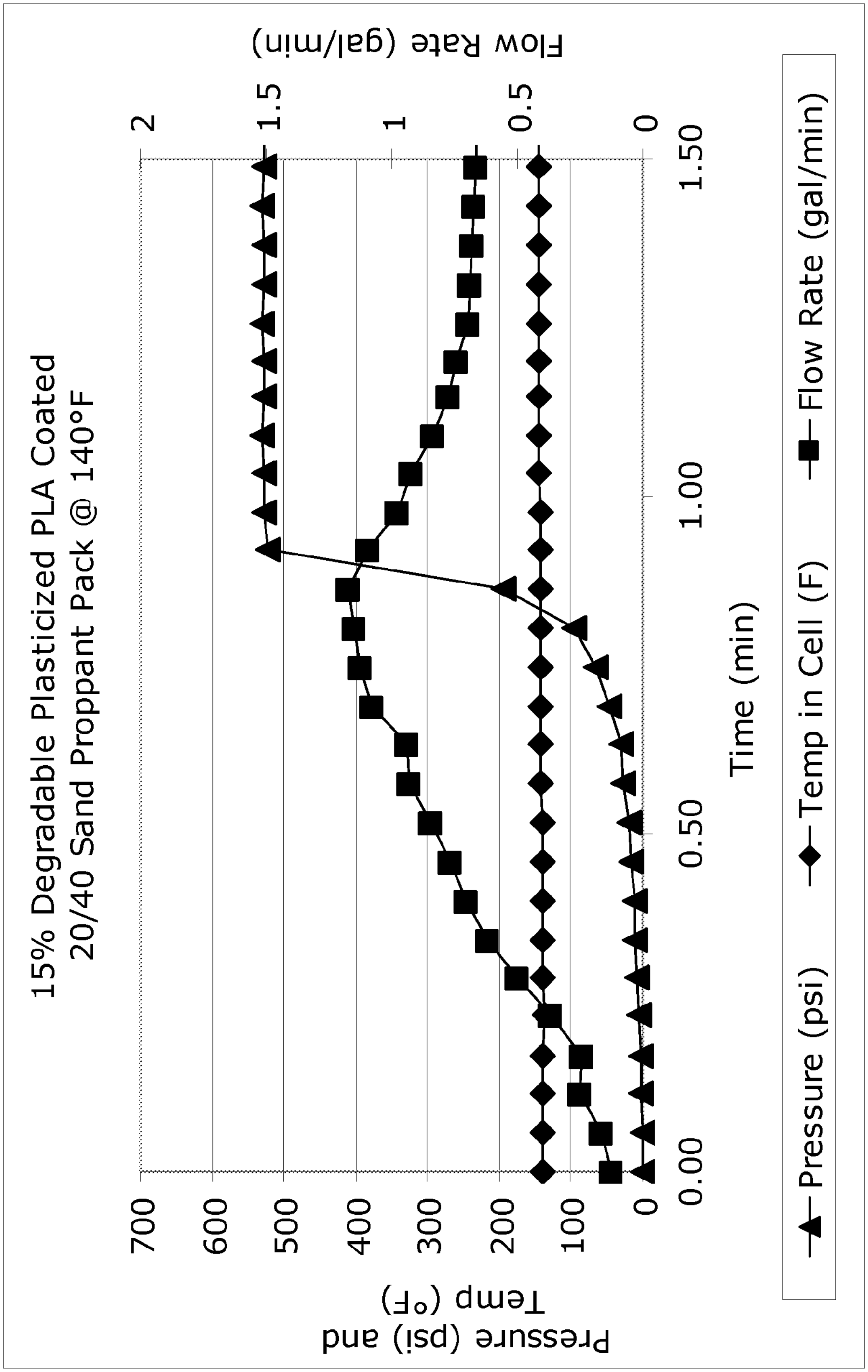
15% Degradable Plasticized PLA Coated
20/40 Sand Proppant Pack @ 140°F
Pressure (psi) and
Temp (°F)
700
600
500
400
300
200
100
0
Flow Rate (gal/min)
2
1.5
1
0.5
0
Time (min)
0.00
0.50
1.00
1.50
Pressure (psi)
Temp in Cell (F)
Flow Rate (gal/min)

FIG. 3

METHOD OF TREATING ULTRA-LOW PERMEABLE SUBTERRANEAN FORMATIONS USING PROPPANT PARTICULATES COATED WITH DEGRADABLE MATERIAL

BACKGROUND

[0001] The present invention relates to methods of propping and increasing the complexity of fractures in ultra-low permeable subterranean formations using proppant coated with degradable material.

[0002] Oil and gas production is typically achieved by drilling a wellbore into a subterranean formation having a reservoir containing oil and/or gas. After the wellbore is drilled, a casing (e.g., hollow piping) having a slightly smaller diameter than the wellbore is placed within the wellbore. Generally, the casing is held into place by pumping hydraulic cement into the annulus between the wellbore and the casing. The hydraulic cement is set in the annular space, forming a hardened, impermeable cement sheath that lends support to the casing. The wellbore then may be stimulated to produce oil and/or gas by hydraulic fracturing.

[0003] In hydraulic fracturing treatments, a fracturing fluid is pumped into the wellbore at a rate and pressure sufficient to create or extend a permeable flow path, or "fracture," within the subterranean formation generally perpendicular to the wellbore. A newly-created or newly-extended fracture will tend to close after the pumping of the fracturing fluid is stopped. To prevent the fracture from closing, a large volume of solid particulates, or "proppant" (also referred to as "proppant particulates"), are typically placed in the fracture to keep the fracture propped open and provide higher fluid conductivity of the formation. The proppant may be suspended in the fracturing fluid or a subsequently pumped fluid, where they are deposited into a fracture to form a "proppant pack" of tightly packed proppant. The proppant pack props the fracture in an open condition while allowing fluid flow through the permeable interstitial spaces between the individual proppant that make up the proppant pack. The proppant pack provides a higher permeability flow path than for oil and/or gas into the wellbore than the subterranean formation matrix itself, thus aiding to increase the productivity of the formation.

[0004] Ultra-low permeability formations, such as shale formations, typically have a naturally occurring network of interconnected small fractures, referred to as "fracture complexity." As used herein, the term "ultra-low permeability formation" refers to formations having a matrix permeability of less than about 1 microDarcy. The fracture complexity of ultra-low permeability formations may be enhanced by hydraulic fracturing techniques. Generally, hydraulic fracturing of ultra-low permeability formations involves pumping a minimally viscous fracturing fluid and a low concentration of proppant into the formation. The proppant form proppant packs within the interconnected small fractures in the formation. However, hydraulic fracturing treatments in ultra-low permeability formations typically enhance only more prominent, or larger, fractures within the fracture complexity network. Therefore, the proppant are typically packed into only a few of the fractures within the fracture complexity network, rather than taking advantage of the already present multitudinous interconnected fractures. As such, the productivity of the formation is not optimized. Therefore, a method of fracturing and propping an ultra-low permeability formation that increases the natural fracture complexity of the fracture complexity network may be of benefit to one of ordinary skill in the art.

SUMMARY OF THE INVENTION

[0005] The present invention relates to methods of propping and increasing the complexity of fractures in ultra-low permeable subterranean formations using proppant coated with degradable material.

[0006] In some embodiments, the present invention provides a method of treating an ultra-low permeability subterranean formation having a fracture complexity comprising interconnected fractures comprising: providing a fracturing fluid comprising a base fluid and coated proppant, wherein the coated proppant comprise proppant coated with a degradable material; introducing the fracturing fluid into the ultra-low permeability subterranean formation at a rate and pressure above a fracture gradient of the ultra-low permeability subterranean formation; placing the coated proppant into at least one fracture within the interconnected fractures so as to form a temporarily impermeable proppant pack comprising the coated proppant therein and reduce or prevent the extension of the at least one fracture; reducing the pressure below the fracture gradient; and degrading the degradable material coating the coated proppant so as to cause the temporarily impermeable proppant pack to become a permeable proppant pack.

[0007] In other embodiments, the present invention provides a method of treating an ultra-low permeability subterranean formation having a fracture complexity comprising interconnected fractures comprising: providing a fracturing fluid comprising a base fluid, coated proppant, and degradable particulates, wherein the coated proppant comprise proppant coated with a degradable material; introducing the fracturing fluid into the ultra-low permeability subterranean formation at a rate and pressure above a fracture gradient of the ultra-low permeability subterranean formation; placing the coated proppant and the degradable particulates into at least one fracture within the interconnected fractures so as to form a temporarily impermeable proppant pack comprising the coated proppant and the degradable particulates therein and reduce or prevent the extension of the at least one fracture; reducing the pressure below the fracture gradient; and degrading the degradable particulates and the degradable material coating the coated proppant so as to cause the temporarily impermeable proppant pack to become a permeable proppant pack.

[0008] In still other embodiments, the present invention provides a method of treating an ultra-low permeability subterranean formation having a fracture complexity comprising interconnected fractures comprising: providing a fracturing fluid comprising a base fluid, coated proppant, and coated degradable particulates, wherein the coated proppant comprise proppant coated with a first degradable material, and wherein the coated degradable particulates comprise degradable particulates coated second degradable material; introducing the fracturing fluid into the ultra-low permeability subterranean formation at a rate and pressure above a fracture gradient of the ultra-low permeability subterranean formation; placing the coated proppant and the coated degradable particulates into at least one fracture of the interconnected fractures so as to form a temporarily impermeable proppant pack comprising the coated proppant and the coated degradable particulates therein and reduce or prevent the extension of the fracture; reducing the pressure below the fracture gradient; and degrading the first and second degradable material coating the coated proppant and the coated degradable particulates, so as to cause the temporarily impermeable proppant pack to become a permeable proppant pack.

[0009] The features and advantages of the present invention will be readily apparent to those skilled in the art upon a reading of the description of the preferred embodiments that follows.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] The following figures are included to illustrate certain aspects of the present invention, and should not be viewed as exclusive embodiments. The subject matter is capable of considerable modifications, alterations, combinations, and equivalents in form and function, as will occur to those skilled in the art and having the benefit of this disclosure.

[0011] FIG. **1** illustrates the ability of proppant coated with a degradable, plasticized material at a temperature near or slightly above the glass transition temperature of the degradable, plasticized material to form an impermeable proppant pack, as described in Example 1.

[0012] FIG. **2** shows the ability of proppant coated with a degradable, non-plasticized material at a temperature near or slightly above the glass transition temperature of the degradable, non-plasticized material to form an impermeable proppant pack, as described in Example 2.

[0013] FIG. **3** demonstrates the ability of proppant coated with a degradable, plasticized material at a temperature above the glass transition temperature of the degradable, plasticized material to form an impermeable proppant pack, as described in Example 3.

DETAILED DESCRIPTION

[0014] The present invention relates to methods of propping and increasing the complexity of fractures in ultra-low permeable subterranean formations using proppant coated with degradable material.

[0015] In particular, the present invention provides methods of forming temporarily impermeable proppant packs by introducing a fracturing fluid comprising proppant coated with degradable material into the formation, so as to force additional fracturing fluid to increase the fracture complexity of the formation. As used herein, the term "impermeable proppant pack" refers to a proppant pack capable of reducing flow by at least 75% compared to a proppant pack having no degradable material coating of the same base size distribution at a differential pressure of at least about 100 psi, and more preferably at a differential pressure of from about 250 psi to about 500 psi. The temporarily impermeable proppant pack is characterized by a lower flow capacity than small fractures having no proppant therein, causing additional fracturing fluid to flow into those areas and form other temporarily impermeable proppant packs, thus increasing fracture complexity rather than simply extending fracture planes during hydraulic fracturing treatments. Often, the temporarily impermeable proppant pack is formed at the far-field region of a fracture. As used herein, the term "far-field region" of a fracture is considered an area of the fracture at least 5 feet from the wellbore. In preferred embodiments, the temporarily impermeable proppant pack is formed in a section of the fracture at least 10 feet from the wellbore. In event more preferred embodiments, the temporarily impermeable proppant pack is formed in a section of the fracture at least 50 feet from the wellbore. After the fracture complexity is increased, the degradable material coating the proppant is degraded so as to cause the proppant pack to become a permeable proppant pack and allow produced hydrocarbons to flow therethrough. As used herein, the term "permeable proppant pack" refers to a proppant pack capable of allowing at least 75% flow compared to a proppant pack having no degradable material coating of the same base size distribution at a differential pressure of at least about 500 psi.

[0016] In one embodiment, the present invention provides a method of propping an ultra-low permeability formation having interconnected fractures and increasing the fracture complexity of the formation. A fracturing fluid is provided comprising a base fluid and proppant coated with a degradable material. The fracturing fluid is introduced into the ultra-low permeability subterranean formation at a rate and pressure above the fracture gradient of the formation so as to place the coated proppant within a fracture of the interconnected fracture network and form a temporarily impermeable proppant pack and reduce or prevent the extension of the fracture. The pressure is then reduced below the fracture gradient and the degradable material coated on the proppant forming the proppant pack is degraded so as to become a permeable proppant pack through which produced fluids may flow. As used herein, the term "fracture gradient" refers to the pressure required to induce or extend fractures in a subterranean formation. Introducing the treatment fluid of the present invention into an ultra-low permeability subterranean formation above the fracture gradient is intended to increase stimulated fracture volume.

[0017] Suitable base fluids for use in any of the treatment fluids of the present invention requiring a base fluid may include, but are not limited to, oil-based fluids; aqueous-based fluids; aqueous-miscible fluids; water-in-oil emulsions; or oil-in-water emulsions. Suitable oil-based fluids may include alkanes; olefins; aromatic organic compounds; cyclic alkanes; paraffins; diesel fluids; mineral oils; desulfurized hydrogenated kerosenes; and any combination thereof. Suitable aqueous-based fluids may include fresh water; saltwater (e.g., water containing one or more salts dissolved therein); brine (e.g., saturated salt water); seawater; and any combination thereof. Suitable aqueous-miscible fluids may include, but not be limited to, alcohols (e.g., methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, isobutanol, and t-butanol); glycerins; glycols (e.g., polyglycols, propylene glycol, and ethylene glycol); polyglycol amines; polyols; any derivative thereof; any in combination with salts (e.g., sodium chloride, calcium chloride, calcium bromide, zinc bromide, potassium carbonate, sodium formate, potassium formate, cesium formate, sodium acetate, potassium acetate, calcium acetate, ammonium acetate, ammonium chloride, ammonium bromide, sodium nitrate, potassium nitrate, ammonium nitrate, ammonium sulfate, calcium nitrate, sodium carbonate, and potassium carbonate); any in combination with an aqueous-based fluid; and any combination thereof. Suitable water-in-oil emulsions, also known as invert emulsions, may have an oil-to-water ratio from a lower limit of greater than about 50:50, 55:45, 60:40, 65:35, 70:30, 75:25, or 80:20 to an upper limit of less than about 100:0, 95:5, 90:10, 85:15, 80:20, 75:25, 70:30, or 65:35 by volume in the base fluid, where the amount may range from any lower limit to any upper limit and encompass any subset therebetween. Examples of suitable invert emulsions include those disclosed in U.S. Pat. No. 5,905,061 entitled "Invert Emulsion Fluids Suitable for Drilling" filed on May 23, 1997, U.S. Pat. No. 5,977,031 entitled "Ester Based Invert Emulsion Drilling Fluids and Muds Having Negative Alkalinity" filed on Aug. 8, 1998, U.S. Pat. No. 6,828,279 entitled "Biodegradable Surfactant for Invert Emulsion Drilling Fluid" filed on Aug. 10, 2001, U.S. Pat. No. 7,534,745 entitled "Gelled Invert Emulsion Compositions Comprising Polyvalent Metal Salts of an Organophosphonic Acid Ester or an Organophosphinic Acid and Methods of Use and Manufacture" filed on May 5, 2004, U.S. Pat. No. 7,645,723 entitled "Method of Drilling Using Invert Emulsion Drilling Fluids" filed on Aug. 15, 2007, and U.S. Pat. No. 7,696,131 entitled "Diesel Oil-Based Invert Emulsion Drilling Fluids and Methods of Drilling Boreholes" filed on Jul. 5, 2007, each of which are incorporated herein by reference in their entirety. It should be noted that for water-in-oil and oil-in-water emulsions, any mixture of the above may be used including the water being and/or comprising an aqueous-miscible fluid.

[0018] In preferred embodiments, the base fluid used in the treatment fluids of the present invention is an aqueous-based fluid. Often large volumes of treatment fluid are required in the present invention and aqueous-based fluids are typically relatively low in cost compared to the other base fluids suitable for use in the present invention. In addition, aqueous-based fluids may pose the least danger of damaging oil or gas reservoirs and the environment.

[0019] In some embodiments of the present invention, the treatment fluids may further comprise any additive suitable for use in a subterranean formation. The additive may be used in order to enhance the qualities of the treatment fluid. Suitable additives may include, but are not limited to, a weighting agent; a fluid loss control agent; an emulsifier; a dispersion aid; a corrosion inhibitor; an emulsion thinner; an emulsion thickener; a viscosifying agent; a gelling agent; a surfactant; a lost circulation material; a foaming agent; a gas; a pH control additive; a breaker; a biocide; a crosslinker; a stabilizer; a chelating agent; a scale inhibitor; a gas hydrate inhibitor; a mutual solvent; an oxidizer; a friction reducer; a clay stabilizing agent; and any combinations thereof.

[0020] The proppant that may be used in the treatment fluids of the present invention may be any material suitable for use in a stimulation operation. Proppant suitable for use in the methods of the present invention may be of any size and shape combination known in the art as suitable for use in a subterranean operation. In preferred embodiments, the proppant for use in the methods of the present invention have an upper size range of about 400 U.S. Standard Mesh. More preferably, the proppant particulate have a graded size range of about −50/+200 U.S. Standard Mesh. Most preferably, the proppant have a size range of about −70/+140 U.S. Standard Mesh. Typically, the proppant for use in forming the proppant packs of the present invention have a median particulate size of about 100 U.S. Standard Mesh, and more preferably of about 50 U.S. Standard Mesh.

[0021] In some embodiments of the present invention, it may be desirable to use substantially spherical proppant. In other embodiments of the present invention, it may be desirable to use substantially non-spherical proppant. Suitable substantially non-spherical proppant may be cubic, polygonal, fibrous, or any other non-spherical shape. Such substantially non-spherical proppant may be, for example, cubic-shaped; rectangular-shaped; rod-shaped; ellipse-shaped; cone-shaped; pyramid-shaped; or cylinder-shaped. That is, in embodiments wherein the proppant are substantially non-spherical, the aspect ratio of the material may range such that the material is fibrous to such that it is cubic; octagonal; or any other configuration. Generally, the proppant may have an aspect ration of less than about 5:1.

[0022] Suitable material compositions for the proppant of the present invention include, but are not limited to, sand; bauxite; ceramic materials; glass materials; polymer materials (such as ethylene vinyl acetate or composite materials); polytetrafluoroethylene materials; nut shell pieces; cured resinous particulates comprising nut shell pieces; seed shell pieces; cured resinous particulates comprising seed shell pieces; fruit pit pieces; cured resinous particulates comprising fruit pit pieces; wood, composite particulates; and combinations thereof. Suitable composite particulates may comprise a binder and a filler material wherein suitable filler materials include silica; alumina; fumed carbon; carbon black; graphite; mica; titanium dioxide; barite; meta-silicate; calcium silicate; kaolin; talc; zirconia; boron; fly ash; hollow glass microspheres; solid glass; and combinations thereof. Suitable proppant particles for use in conjunction with the present invention may be any known shape of material, including substantially spherical materials; fibrous materials; polygonal materials (such as cubic materials); and combinations thereof. Proppant may be present in the treatment fluids of the present invention in an amount from about 0.1 pounds per gallon to about 4 pounds per gallon. The proppant of the present invention may be present in the treatment fluids in the range of about 5% to about 10% by volume.

[0023] The proppant of the present invention are coated with a degradable material. The degradable material upon a triggering effect, is degraded in order to form a permeable proppant pack through which produced fluids may flow. The degradable material causes the interstitial spaces between the individual proppant to become unclogged where they were previously clogged with the degradable material. The degradable materials of the present invention are capable of undergoing an irreversible degradation downhole. As used herein, the term "irreversible" means that the degradable material once degraded should not recrystallize or reconsolidate while downhole.

[0024] Degradation of the degradable materials of the present invention may be achieved by a chemical or thermal reaction or a reaction induced by radiation, for example. The degradable material may be degraded by any mechanism including, but not limited to, hydrolysis, hydration followed by dissolution, dissolution, decomposition, or sublimation. Where degradation of the degradable materials requires fluid or water, the methods of the present invention allow sufficient fluid seepage through the impermeable proppant packs of the present invention to permit degradation. In some embodiments, it may be desirable to include a water-releasing agent in the fracturing fluid to facilitate the release of water under downhole conditions and aiding in degrading the degradable materials of the present invention. The water releasing agent may be any material capable of releasing water upon a chemical reaction (e.g., internal reaction or reaction with the subterranean formation). An example of a suitable water releasing agent may be activated carbon.

[0025] Nonlimiting examples of degradable materials for use in coating the proppant of the present invention include, but are not limited to, aromatic polyesters and aliphatic polyesters. Such polyesters may be linear, graft, branched, crosslinked, block, dendritic, homopolymers, random, and the like.

[0026] Suitable degradable polymers for use as the degradable materials for use in coating the proppant of the present invention include, but are not limited to, a poly(hydroxyl alkanoate); a poly(alpha-hydroxy) acid (e.g., polylactic acid, polyglycolic acid, polylactide, and polyglycolide); a poly(beta-hydroxy alkanoate); a poly(omega-hydroxy alkanoate) (e.g., poly(beta-propiolactone) and poly(E-caprolactone)); a poly(alkylene dicarboxylate (e.g., poly(ethylene succinate), poly(butylene succinate), and poly(butylene succinate-co-butylene adipate)); a polyanhydride (e.g., poly(adipic anhydride)); a poly(orthoester); a polycarbonate (e.g., poly(trimethylene carbonate) and poly(dioxepan-2-one)); an aliphatic polyester; a poly(lactide); a poly(glycolide); a poly(hydroxybutyrate); a poly(anhydride); an aliphatic polycarbonate; a poly(amino acid); a poly(ethylene oxide); a polyphosphazene; any derivatives thereof; and any combinations thereof. Of these suitable polymers, poly(lactides); polylactic acid; aliphatic polyesters; and polyanhydrides are preferred. Derivatives that have added functional groups may also be used as degradable materials for use in the present invention. Blends of certain degradable materials may also be suitable. One example of a suitable blend of materials is a blend of poly(lactic acid) and boric oxide.

[0027] In choosing the appropriate degradable material, one should consider the degradation products that will result. These degradation products should not adversely affect other operations or components and may even be selected to improve the long-term performance/conductivity of the propped fracture network of the ultra-low permeability subterranean formation. The choice of degradable material also can depend, at least in part, on the conditions of the well, (e.g., wellbore temperature, salinity, pH, and the like). By way of nonlimiting example, lactides have been found to be suitable for lower temperature wells, including those within the range of 60° F. to 150° F., and polylactides have been found to be suitable for well bore temperatures above this range. Also, poly(lactic acid) may be suitable for higher temperature wells. Some stereoisomers of poly(lactide) or mixtures of such stereoisomers may be suitable for even higher temperature applications.

[0028] In some embodiments a preferable result is achieved if the degradable material degrades slowly over time as opposed to instantaneously. Even more preferable results have been obtained when the degradable material does not begin to degrade until after the proppant pack has developed some compressive strength. The slow degradation of the degradable material, in situ, helps to maintain the stability of the proppant pack.

[0029] A plasticizer may be included in the degradable materials of the present invention so as to provide certain desirable characteristics such as, for example, tackiness or stickiness. In addition, the plasticizers may lower the glass transition temperature of the degradable material so as to lower the temperature at which the degradable material will become tacky, for example. As used herein, the term “glass transition temperature” refers to the temperature at which a temperature-sensitive solid becomes soft upon heading. Therefore, a plasticizer may be preferably incorporated into the degradable materials of the present invention, particularly when the degradable material has a particularly high glass transition temperature in comparison to the temperature of the ultra-low permeability formation in which it is to be used. The plasticizers, if used, are preferably at least intimately incorporated within the degradable material. An example of a suitable plasticizer for poly(lactic acid) would include oligomeric lactic acid. Examples of plasticizers that may be useful in some embodiments of the present invention include, but are not limited to, polyethylene glycol; polyethylene oxide; oligomeric lactic acid; citrate esters (such as tributyl citrate oligomers, triethyl citrate, acetyltributyl citrate, and acetyltriethyl citrate); glucose monoesters; partially fatty acid esters; polyethylene glycol monolaurate; triacetin; poly(e-caprolactone); poly(hydroxybutyrate); glycerin-l-benzoate-2,3-dilaurate; glycerin-2-benzoate-l,3-dilaurate; bis(butyl diethylene glycol)adipate; ethylphthalylethyl glycolate; glycerin diacetate monocaprylate; diacetyl monoacyl glycerol; polypropylene glycol; poly(propylene glycol)dibenzoate; dipropylene glycol dibenzoate; glycerol; ethyl phthalyl ethyl glycolate; poly(ethylene adipate)distearate; di-iso-butyl adipate; any derivatives thereof; and combinations thereof. The choice of an appropriate plasticizer will depend on the particular degradable material utilized.

[0030] The degradable material composition may be coated onto the proppant of the present invention by any means known in the art. For example, the degradable material composition may be coated onto the proppant by spraying, atomizing, liquid mixing, or any other suitable means. Additionally, the degradable material composition may be pre-coated onto the proppant prior to performing the methods of the present invention or “on-the-fly” at the well site.

[0031] In some embodiments, a degradable particulate, uncoated or coated with a degradable material, may be included in the treatment fluids so as to form a portion of the proppant pack with the coated proppant. The degradable particulates may degrade and leave voids behind so as to increase the permeability of the proppant pack beyond that achieved by degrading the degradable material coated upon the proppant alone. The degradable particulates may preferably differ in composition from the degradable material coating either the proppant or the degradable particulates. This may be preferred so as to control degradation rates and allow certain degradable compositions to degrade prior to or faster than other degradable compositions of the present invention. For example, it may be desirable that the degradable material coated on the proppant and/or coated onto the degradable particulates degrade prior to the degradation of the degradable particulates themselves. This may increase the permeability of the proppant pack slowly over time.

[0032] The degradable particulates may be coated with any degradable material composition (e.g., a degradable material and a plasticizer) used to coat the proppant. Additionally, the degradable particulates for use in the present invention may be a solid particulate composed of any of the degradable material compositions suitable for coating on the proppant or the degradable particulates. In addition to those degradable materials capable of coating a proppant particulate or degradable particulate as well as forming a degradable solid particulate alone for use in the methods of the present invention, the degradable particulates may be composed of a dehydrated salt. For example, a particulate solid anhydrous borate material that degrades over time may be suitable. Specific examples of particulate solid anhydrous borate materials that may be used include, but are not limited to, anhydrous sodium tetraborate (also known as anhydrous borax) and anhydrous boric acid. These anhydrous borate materials are only slightly soluble in water. However, with time and heat in a subterranean environment, the anhydrous borate materials react with the surrounding aqueous fluid and are hydrated. The resulting hydrated borate materials are highly soluble in water as compared to anhydrous borate materials and as a result degrade in the aqueous fluid. In some instances, the total time required for the anhydrous borate materials to degrade in an aqueous fluid is in the range of from about 8 hours to about 72 hours depending upon the temperature of the subterranean zone in which they are placed. Other examples include organic or inorganic salts like acetate trihydrate. Dehydrated salts may also be suitable for higher temperature wells and are preferably coated with a degradable material to delay the contact of the dehydrated salt with water and, thus, its degradation.

[0033] In some embodiments of the present invention, from about 10% to about 70% of the total proppant used to form the proppant pack are degradable particulates. In other embodiments, from about 20% to about 50% of the total proppant used to form the proppant pack are degradable particulates. In still other embodiments, from about 25% to about 40% of the total proppant used to form the proppant pack are degradable particulates. One of ordinary skill in the art, with the benefit of this disclosure will recognize an optimum concentration of degradable material that provides desirable values in terms of enhanced conductivity or permeability without undermining the stability of the high porosity fracture itself.

[0034] In some embodiments, a consolidating agent may be included to aid in binding individual proppant and/or degradable particulates together to form the proppant pack. A consolidating agent may be preferably used when a plasticizer is not included in the degradable material coating the proppant, or, when applicable, the degradable material coating the degradable particulates or the degradable particulates themselves. Additionally, a consolidating agent may be suitable to enhance the characteristics of the plasticizers of the present invention, when applicable. Suitable consolidating agents may include any consolidating agent suitable for use in stimulation operations. Nonlimiting examples of suitable consolidating agents include, but are not limited to, non-aqueous tackifying agents; aqueous tackifying agents; emulsified tackifying agents; silyl-modified polyamide compounds; resins; crosslinkable aqueous polymer compositions; polymerizable organic monomer compositions; consolidating agent emulsions; zeta-potential modifying aggregating compositions; silicon-based resins; binders; any derivatives thereof; and any combinations thereof. The consolidating agent may be present in the thermal thinning resistant treatment fluids of the present invention in an amount from about 0.1% to about 10% by weight of the combined proppant particulate and degradable particulate, if applicable. In preferred embodiments, the consolidating agent may be present in the treatment fluids of the present invention from about 1% to about 5% by weight of the combined proppant particulate and degradable particulate, if applicable. It is within the ability of one skilled in the art, with the benefit of this disclosure, to determine the need and type and amount of consolidating agent to include in the methods of the present invention to achieve the desired results.

EXAMPLES

Example 1

[0035] In this example, the ability of 20/40 sand coated with 15% degradable plasticized polylactic acid (PLA) was evaluated for its ability to produce an impermeable proppant pack. The degradable plasticized PLA was prepared by blending 45 grams of polylactic acid with 6.75 grams of tributyl citrate plasticizer in a Brabender Twin-Screw Mixer at 135° C. The degradable plasticized PLA was blended for 2 min at 100 RPM, and then chopped into 1 mm size particles for ease of handling. The glass transition temperature of the degradable plasticized PLA was determined by differential scanning calorimetry (DSC) using a Q200 from TA Instruments. The DSC scans were performed initially at temperatures −50° C. to 200° C. at 10° C. per min, then the temperature was again reduced to −50° C., and finally raised back to 200° C. at 10° C. per min. The glass transition temperature of the degradable plasticized PLA was determined to be 33° C. based on the second heating cycle.

[0036] Degradable plasticized PLA coated proppant were prepared by coating 15% of the degradable plasticized PLA by dry weight of 20/40 sand. To 400 grams of 20/40 sand (proppant particulate) heated to 280° C. for 30 min, 60 grams of the degradable plasticized PLA was added and vigorously stirred. After the mixture was well stirred, cool water was added to cause the degradable plasticized PLA to coat or adhere to the sand and form degradable plasticized PLA coated proppant. The degradable plasticized PLA coated proppant were filtered through a funnel and dried in air.

[0037] The ability of the degradable plasticized PLA coated proppant to form an impermeable proppant pack was evaluated using a 1" ID cell packed with 150 grams of the degradable plasticized PLA coated proppant.

[0038] Through the cell packed with degradable plasticized PLA coated proppant, water preheated to 43° C. (110° F.) was flowed at a rate of 1.3 gal/min. After 8 minutes, the pressure within the cell increased from approximately 0 psi to approximately 520 psi, indicating that an impermeable proppant pack was formed. Because the glass transition temperature of the degradable plasticized PLA is 33° C., the degradable plasticized PLA was softened at the treatment temperature of 43° C. and served to plug the proppant pack. The pressure, flow rate, and cell temperature results are shown in FIG. **1**.

Example 2

[0039] In this example, the ability of 20/40 sand coated with 15% degradable non-plasticized polylactic acid (PLA) was evaluated for its ability to produce an impermeable proppant pack. The glass transition temperature of the degradable non-plasticized PLA was determined by differential scanning calorimetry (DSC) using a Q200 from TA Instruments. The DSC scans were performed initially at temperatures −50° C. to 200° C. at 10° C. per min, then the temperature was again reduced to −50° C., and finally raised back to 200° C. at 10° C. per min. The glass transition temperature of the degradable non-plasticized PLA was determined to be 64° C. based on the second heating cycle.

[0040] The ability of the degradable non-plasticized PLA coated proppant to form an impermeable proppant pack was evaluated using a 1" ID cell packed with 150 grams of the degradable non-plasticized PLA coated proppant.

[0041] Through the cell packed with degradable non-plasticized PLA coated proppant, water preheated to 60° C. (140° F.) was flowed at a rate of 1.3 gal/min. After 8 minutes, the pressure within the cell increased from approximately 0 psi to approximately 520 psi, indicating that an impermeable proppant pack was formed. The glass transition temperature of the degradable non-plasticized PLA of 64° C. is only slightly higher than the treatment temperature of 60° C. Nevertheless, after 8 minutes, the degradable non-plasticized PLA was softened and able to plug the proppant pack. The pressure, flow rate, and cell temperature results are shown in FIG. **2**

Example 3

[0042] Through a 1" ID cell packed with 150 grams of the coated proppant as prepared in Example 1, water preheated to 60° C. (140° F.) was flowed at a rate of 1.0 gal/min. After 1 minute, the pressure within the cell increased from approximately 0 psi to approximately 520 psi, indicating that an impermeable proppant pack was formed. Because the glass transition temperature of the degradable plasticized PLA coating mixture is 33° C., the degradable plasticized PLA coating mixture was softened quickly at the treatment temperature of 60° C. and served to plug the proppant pack. Additionally, the flow rate quickly dropped from 1.0 gallons per minute to 0.65 gallons per minute due to the plugging. The pressure, flow rate, and cell temperature results are shown in FIG. **3**.

[0043] Therefore, the present invention is well adapted to attain the ends and advantages mentioned as well as those that are inherent therein. The particular embodiments disclosed above are illustrative only, as the present invention may be modified and practiced in different but equivalent manners apparent to those skilled in the art having the benefit of the teachings herein. Furthermore, no limitations are intended to the details of construction or design herein shown, other than as described in the claims below. It is therefore evident that the particular illustrative embodiments disclosed above may be altered, combined, or modified and all such variations are considered within the scope and spirit of the present invention. The invention illustratively disclosed herein suitably may be practiced in the absence of any element that is not specifically disclosed herein and/or any optional element disclosed herein. While compositions and methods are described in terms of "comprising," "containing," or "including" various components or steps, the compositions and methods can also "consist essentially of" or "consist of" the various components and steps. All numbers and ranges disclosed above may vary by some amount. Whenever a numerical range with a lower limit and an upper limit is disclosed, any number and any included range falling within the range is specifically disclosed. In particular, every range of values (of the form, "from about a to about b," or, equivalently, "from approximately a to b," or, equivalently, "from approximately a-b") disclosed herein is to be understood to set forth every number and range encompassed within the broader range of values. Also, the terms in the claims have their plain, ordinary meaning unless otherwise explicitly and clearly defined by the patentee. Moreover, the indefinite articles "a" or "an," as used in the claims, are defined herein to mean one or more than one of the element that it introduces. If there is any conflict in the usages of a word or term in this specification and one or more patent or other documents that may be incorporated herein by reference, the definitions that are consistent with this specification should be adopted.

The invention claimed is:

1. A method of treating an ultra-low permeability subterranean formation having a fracture complexity comprising interconnected fractures comprising:

providing a fracturing fluid comprising a base fluid and coated proppant,

wherein the coated proppant comprise proppant coated with a degradable material;

introducing the fracturing fluid into the ultra-low permeability subterranean formation at a rate and pressure above a fracture gradient of the ultra-low permeability subterranean formation;

placing the coated proppant into at least one fracture of the interconnected fractures so as to form a temporarily impermeable proppant pack comprising the coated proppant therein and reduce or prevent the extension of the at least one fracture;

reducing the pressure below the fracture gradient; and

degrading the degradable material coating the coated proppant so as to cause the temporarily impermeable proppant pack to become a permeable proppant pack.

2. The method of claim **1** wherein the temporarily impermeable proppant pack is capable of reducing flow by at least 75% at a differential pressure of at least about 100 psi.

3. The method of claim **1** wherein the permeable proppant pack is capable of allowing at least 75% flow at a differential pressure of at least about 500 psi.

4. The method of claim **1** wherein the treatment fluid further comprises a consolidating agent.

5. The method of claim **1** wherein the degradable material is selected from the group consisting of a poly(hydroxyl alkanoate); a poly(alpha-hydroxy) acid; a poly(beta-hydroxy alkanoate); a poly(omega-hydroxy alkanoate); a poly(alkylene dicarboxylate; a polyanhydride; a poly(orthoester); a polycarbonate; an aliphatic polyester; a poly(lactide); a poly (glycolide); a poly(hydroxybutyrate); a poly(anhydride); an aliphatic polycarbonate; a poly(amino acid); a poly(ethylene oxide); a polyphosphazene; any derivatives thereof; and any combinations thereof.

6. The method of claim **1** wherein the degradable material further comprises a plasticizer selected from the group consisting of polyethylene glycol; polyethylene oxide; oligomeric lactic acid; a citrate ester; a glucose monoester; a partially fatty acid ester; polyethylene glycol monolaurate; triacetin; poly(e-caprolactone); poly(hydroxybutyrate); glycerin-1-benzoate-2,3-dilaurate; glycerin-2-benzoate-l,3-dilaurate; bis(butyl diethylene glycol)adipate; ethylphthalylethyl glycolate; glycerin diacetate monocaprylate; diacetyl monoacyl glycerol; polypropylene glycol; poly(propylene glycol) dibenzoate; dipropylene glycol dibenzoate; glycerol; ethyl phthalyl ethyl glycolate; poly(ethylene adipate)distearate; di-iso-butyl adipate; any derivatives thereof; and combinations thereof.

7. A method of treating an ultra-low permeability subterranean formation having a fracture complexity comprising interconnected fractures comprising:

providing a fracturing fluid comprising a base fluid, coated proppant, and degradable particulates,

wherein the coated proppant comprise proppant coated with a degradable material;

introducing the fracturing fluid into the ultra-low permeability subterranean formation at a rate and pressure above a fracture gradient of the ultra-low permeability subterranean formation;

placing the coated proppant and the degradable particulates into at least one fracture of the interconnected fractures so as to form a temporarily impermeable proppant pack comprising the coated proppant and the degradable particulates therein and reduce or prevent the extension of the fracture;

reducing the pressure below the fracture gradient; and

degrading the degradable particulates and the degradable material coating the coated proppant so as to cause the temporarily impermeable proppant pack to become a permeable proppant pack.

8. The method of claim **7** wherein the temporarily impermeable proppant pack is capable of reducing flow by at least 75% at a differential pressure of at least about 100 psi.

9. The method of claim **7** wherein the permeable proppant pack is capable of allowing at least 75% flow at a differential pressure of at least about 500 psi.

10. The method of claim **7** wherein the degradable material is selected from the group consisting of a poly(hydroxyl alkanoate); a poly(alpha-hydroxy) acid; a poly(beta-hydroxy alkanoate); a poly(omega-hydroxy alkanoate); a poly(alkylene dicarboxylate; a polyanhydride; a poly(orthoester); a polycarbonate; an aliphatic polyester; a poly(lactide); a poly (glycolide); a poly(hydroxybutyrate); a poly(anhydride); an aliphatic polycarbonate; a poly(amino acid); a poly(ethylene oxide); a polyphosphazene; any derivatives thereof; and any combinations thereof.

11. The method of claim **7** wherein the degradable material further comprises a plasticizer selected from the group consisting of polyethylene glycol; polyethylene oxide; oligomeric lactic acid; a citrate ester; a glucose monoester; a partially fatty acid ester; polyethylene glycol monolaurate; triacetin; poly(e-caprolactone); poly(hydroxybutyrate); glycerin-l-benzoate-2,3-dilaurate; glycerin-2-benzoate-l,3-dilaurate; bis(butyl diethylene glycol)adipate; ethylphthalylethyl glycolate; glycerin diacetate monocaprylate; diacetyl monoacyl glycerol; polypropylene glycol; poly(propylene glycol) dibenzoate; dipropylene glycol dibenzoate; glycerol; ethyl phthalyl ethyl glycolate; poly(ethylene adipate)distearate; di-iso-butyl adipate; any derivatives thereof; and combinations thereof.

12. The method of claim **7** wherein the degradable particulate is a solid particulate formed from a material selected from the group consisting of a poly(hydroxyl alkanoate); a poly (alpha-hydroxy) acid; a poly(beta-hydroxy alkanoate); a poly (omega-hydroxy alkanoate); a poly(alkylene dicarboxylate; a polyanhydride; a poly(orthoester); a polycarbonate; an aliphatic polyester; a poly(lactide); a poly(glycolide); a poly (hydroxybutyrate); a poly(anhydride); an aliphatic polycarbonate; a poly(amino acid); a poly(ethylene oxide); a polyphosphazene; a dehydrated salt; any derivatives thereof; and any combinations thereof.

13. The method of claim **7** wherein the degradable material coating the proppant differs in composition from the degradable particulate.

14. A method of treating an ultra-low permeability subterranean formation having a fracture complexity comprising interconnected fractures comprising:

providing a fracturing fluid comprising a base fluid, coated proppant, and coated degradable particulates,

wherein the coated proppant comprise proppant coated with a first degradable material, and

wherein the coated degradable particulates comprise degradable particulates coated second degradable material;

introducing the fracturing fluid into the ultra-low permeability subterranean formation at a rate and pressure above a fracture gradient of the ultra-low permeability subterranean formation;

placing the coated proppant and the coated degradable particulates into at least one fracture of the interconnected fractures so as to form a temporarily impermeable proppant pack comprising the coated proppant and the coated degradable particulates therein and reduce or prevent the extension of the fracture;

reducing the pressure below the fracture gradient; and

degrading the first and second degradable material coating the coated proppant and the coated degradable particulates, so as to cause the temporarily impermeable proppant pack to become a permeable proppant pack.

15. The method of claim **14** wherein the temporarily impermeable proppant pack is capable of reducing flow by at least 75% at a differential pressure of at least about 100 psi.

16. The method of claim **14** wherein the permeable proppant pack is capable of allowing at least 75% flow at a differential pressure of at least about 500 psi.

17. The method of claim **14** wherein the first and second degradable material is selected from the group consisting of a poly(hydroxyl alkanoate); a poly(alpha-hydroxy) acid; a poly (beta-hydroxy alkanoate); a poly(omega-hydroxy alkanoate); a poly(alkylene dicarboxylate; a polyanhydride; a poly(orthoester); a polycarbonate; an aliphatic polyester; a poly(lactide); a poly(glycolide); a poly(hydroxybutyrate); a poly(anhydride); an aliphatic polycarbonate; a poly(amino acid); a poly(ethylene oxide); a polyphosphazene; any derivatives thereof; and any combinations thereof.

18. The method of claim **14** wherein the degradable particulate is a solid particulate formed from a material selected from the group consisting of a poly(hydroxyl alkanoate); a poly(alpha-hydroxy) acid; a poly(beta-hydroxy alkanoate); a poly(omega-hydroxy alkanoate); a poly(alkylene dicarboxylate; a polyanhydride; a poly(orthoester); a polycarbonate; an aliphatic polyester; a poly(lactide); a poly(glycolide); a poly (hydroxybutyrate); a poly(anhydride); an aliphatic polycarbonate; a poly(amino acid); a poly(ethylene oxide); a polyphosphazene; any derivatives thereof; and any combinations thereof.

19. The method of claim **14** wherein the first and second degradable material differ in composition from each other.

20. The method of claim **14** wherein the second degradable material differs in composition from the degradable particulates.

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