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(54) Title: WATER SOLUBLE POLYMERS FOR FIBER DISPERSION

(57) Abstract: Methods of treating a subterranean formation include forming a treatment fluid including an aqueous base fluid, a proppant, a water soluble polymer; and hydrophilic fibers having a length of about 100 microns to 10 millimeters. Such methods include placing the treatment fluid in the subterranean formation.



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WATER SOLUBLE POLYMERS FOR FIBER DISPERSION

BACKGROUND

[0001] The present application claims priority to U.S. Provisional Application Serial No. 62/407191 filed October 12, 2016, which is incorporated herein by reference in its entirety.

[0002] Hydrocarbons (*e.g.*, oil, natural gas, etc.) may be obtained from a subterranean formation by drilling a wellbore that penetrates the hydrocarbon-bearing formation. Fracturing operations may be conducted in a wellbore to improve the production of fluids from the formation surrounding the wellbore. A variety of fracturing techniques can be employed, and available systems enable multi-stage stimulation to be performed along the wellbore. Hydraulic fracturing techniques generally involve pumping a fracturing fluid downhole and into the surrounding formation upon its fracture due to the high pressures involved.

[0003] More specifically, hydraulic fracturing techniques inject a fracturing fluid into a wellbore penetrating a subterranean formation thereby forcing the fracturing fluid against the wellbore walls at pressures high enough to crack or fracture the formation, creating or enlarging one or more fractures. Proppant present in the fracturing fluid is then entrained within the fracture by the ingress of the fracturing fluid into the created or enlarged crack, thereby preventing the fracture from closing and thus providing for the improved flow produced fluids from the formation. Proppant is thus used to hold the walls of the fractures apart in order to create conductive paths that can facilitate the flow of fluids through the formation and into the wellbore after pumping has stopped. Being able to place the appropriate proppant at the appropriate concentration to form a suitable proppant pack is thus important for the success of a hydraulic fracturing operation.

[0004] Fibers are incorporated in different oilfield products for various applications. Fibers are used in the fracturing fluids as proppant suspending agents to enable

proppant transport down the wellbore and into the fracture by reduction of proppant settling. Additionally, fibers are used in cement fluids to enhance flexural strength of set cement, avoiding failure due to shear and compressional stresses. Another example of fibers in the oilfield is their use in diversion fluids, as well as loss circulation materials due to their ability to bridge in small openings.

[0005] In some applications, a well dispersed fiber-laden fluid is beneficial. For example, the agglomeration or flocculation of fibers in a treatment fluid may result in an increased rate of screen outs in either the fracture, wellbore or the near-wellbore region. Furthermore, various well treatment and stimulation operations tend to be more successful if the materials, such as fibers, in the treatment fluid are well dispersed and uniformly concentrated therein.

SUMMARY

[0006] This summary is provided to introduce a selection of concepts that are further described below in the detailed description. This summary is not intended to identify key or essential features of the claimed subject matter, nor is it intended to be used as an aid in limiting the scope of the claimed subject matter.

[0007] An aspect includes a treatment fluid including an aqueous base fluid, a proppant, a water soluble polymer; and hydrophilic fibers having a length of about 100 microns to 10 millimeters.

[0008] Another aspect includes methods of treating a subterranean formation including forming a treatment fluid including an aqueous base fluid, a proppant, a water soluble polymer; and hydrophilic fibers having a length of about 100 microns to 10 millimeters. Such methods include placing the treatment fluid in the subterranean formation.

[0009] Other aspects and advantages of the claimed subject matter will be apparent from the following description and the appended claims.

BRIEF DESCRIPTION OF THE DRAWING

- [0010] Various aspects of the present disclosure may be better understood upon reading the detailed description and upon reference to the drawings in which:
- [0011] Figures 1a-c depict optical microscope images of pulp fibers, in accordance with an embodiment of the present disclosure;
- [0012] Figures 2a-d depict bridging test results of pulp fibers, in accordance with an embodiment of the present disclosure;
- [0013] Figures 3a-b depict experimental data using a rheometer, in accordance with an embodiment of the present disclosure;
- [0014] Figures 4a-b depict additional data using a rheometer, in accordance with another embodiment of the present disclosure;
- [0015] Figures 5a-c depict additional optical microscope images of pulp fibers, in accordance with another embodiment of the present disclosure; and
- [0016] Figure 6 depicts experimental data using a TA DHR-3 rheometer, in accordance with another embodiment of the present disclosure.

DETAILED DESCRIPTION

- [0017] Embodiments disclosed herein relate generally to well treatment compositions and methods of using said compositions during well treatment operations. More specifically, embodiments disclosed herein relate to well treatment compositions that include hydrophilic fibers and water soluble polymers and methods employing a water soluble polymer to enhance the dispersion of cellulose fibers.
- [0018] At the outset, it should be noted that in the development of any such actual embodiment, numerous implementation-specific decisions may be made to achieve the developer's specific goals, such as compliance with system related and business related constraints, which will vary from one implementation to another. Moreover, it will be

appreciated that such a development effort might be complex and time consuming but would nevertheless be a routine undertaking for those of ordinary skill in the art having the benefit of this disclosure. In addition, the composition used/disclosed herein can also comprise some components other than those cited. In the summary and this detailed description, each numerical value should be read once as modified by the term "about" (unless already expressly so modified), and then read again as not so modified unless otherwise indicated in context. The term about should be understood as any amount or range within 10% of the recited amount or range (for example, a range from about 1 to about 10 encompasses a range from 0.9 to 11). Also, in the summary and this detailed description, it should be understood that a range listed or described as being useful, suitable, or the like, is intended to include support for any conceivable sub-range within the range at least because every point within the range, including the end points, is to be considered as having been stated. For example, "a range of from 1 to 10" is to be read as indicating each possible number along the continuum between about 1 and about 10. Furthermore, one or more of the data points in the present examples may be combined together, or may be combined with one of the data points in the specification to create a range, and thus include each possible value or number within this range. Thus, (1) even if numerous specific data points within the range are explicitly identified, (2) even if reference is made to a few specific data points within the range, or (3) even when no data points within the range are explicitly identified, it is to be understood (i) that the inventors appreciate and understand that any conceivable data point within the range is to be considered to have been specified, and (ii) that the inventors possessed knowledge of the entire range, each conceivable sub-range within the range, and each conceivable point within the range. Furthermore, the subject matter of this application illustratively disclosed herein suitably may be practiced in the absence of any element(s) that are not specifically disclosed herein.

[0019] Fibers are well known to be used for various purposes in oilfield treatment operations. For example, methods such as fiber assisted transport have been used to improve particle transport in fracturing and wellbore cleanout operations while reducing the amount of other fluid viscosifiers employed.

[0020] Disclosed herein is a treatment fluid, comprising an aqueous base fluid; a proppant; at least one water soluble polymer and hydrophilic fibers having a length of about 100 microns to 10 millimeters. This disclosure also contains methods of treating a subterranean formation by placing the treatment fluid described above in subterranean formation.

[0021] The term "treatment," or "treating," does not imply any particular action by the fluid. For example, a treatment fluid placed or introduced into a subterranean formation subsequent to a leading-edge fluid may be a hydraulic fracturing fluid, an acidizing fluid (acid fracturing, acid diverting fluid), a stimulation fluid, a sand control fluid, a completion fluid, a wellbore consolidation fluid, a remediation treatment fluid, a cementing fluid, a driller fluid, a frac-packing fluid, or gravel packing fluid

[0022] Conventionally, synthetic fibers may be used to assist in the formation of the proppant pillars. However, current manufacturing methods for synthetic fibers have limits to the shortest length achievable for the fibers. However, in order for fibers to be effective within a fracture they must be able to enter the fracture and in some instances the fracture width may be less than the shortest length achievable for synthetic fibers, which makes it difficult for even the smallest synthetic fibers to penetrate into the fracture. For example, a fracture width may decrease the further a fracture extends into a formation. Formations that have fractures with widths smaller than the fiber lengths can present problems for proppant placement within said fractures because the fibers that are attempted to be injected therein tend to be screened out and otherwise accumulate at the mouth or openings of the smaller fracture. Therefore, materials that enable efficient proppant transport into fractures, both large and small, are sought after to improve the efficiency of hydraulic fracturing operations.

[0023] The term "fracturing" refers to the process and methods of breaking down a geological formation and creating a fracture, such as the rock formation around a wellbore, by pumping fluid at very high pressures (pressure above the determined closure pressure of the formation), in order to increase production rates from or injection rates into a hydrocarbon reservoir. The fracturing methods of the present

disclosure may include a composition one or more polymers that may be consolidated to form a polymeric structure upon exposure to a predetermined shear rate in one or more of the treatment fluids, but otherwise use conventional techniques known in the art.

[0024] The term "field" includes land-based (surface and sub-surface) and sub-seabed applications. The term "oilfield," as used herein, includes hydrocarbon oil and gas reservoirs, and formations or portions of formations where hydrocarbon oil and gas are expected but may additionally contain other materials such as water, brine, or some other composition.

[0025] As used herein, the term "polymer" or "oligomer" is used interchangeably unless otherwise specified, and both refer to homopolymers, copolymers, interpolymers, terpolymers, and the like. Likewise, a copolymer may refer to a polymer comprising only two monomers, or comprising at least two monomers, optionally with other additional monomers. When a polymer is referred to as comprising a monomer, the monomer is present in the polymer in the polymerized form of the monomer or in the derivative form of the monomer. However, for ease of reference the phrase comprising the (respective) monomer or the like is used as shorthand.

[0026] HYDROPHILIC FIBER

[0027] In one or more embodiments, disclosed herein is a well treatment fluid composition that includes a hydrophilic fiber and water soluble polymer. For example, the hydrophilic fiber may be a cellulose based fiber such as pulp fiber or microfibrillated cellulose. Cellulose itself constitutes the most abundant renewable and environmentally friendly raw material available on earth. For example, raw materials including wood, recycled paper, and agricultural residues such as bagasse, cereal straw, bamboo, reeds, esparto grass, jute, flax, and sisal all are comprised of cellulose fibers that may be converted into a variety of product including pulp fiber. Depending on the particular application requirements, the raw material processing conditions may be altered to produce a variety of cellulose-based materials that vary in terms of dimension and shape. For example, pulp fibers may generally range from 1 micron to 10

millimeters in length, powdered cellulose may generally range from 1 micron to 1 millimeter, nanofibrillated cellulose may generally range from 100 nanometers to 1 micron, microfibrillated cellulose may generally range from 100 nanometers to 500 microns, and nanocrystalline cellulose may generally range from 50 nanometers to 1000 nanometers. The above length distributions, and any other dimensional details that follow, are all based off of the values for dry fibers. It is to be understood that the hydrophilic fibers of the present disclosure, upon their hydration from a dried state, may elongate and/or swell.

[0028] The worldwide annual output of pulp fiber is about 400 million tons, making pulp fiber one of the most abundant raw materials worldwide. Pulp production begins with raw material preparation, which may include debarking (for wood), chipping, depithing (for bagasse), among others. After the raw material preparation the lignin is stripped from the cellulosic fibers by mechanical, thermal, and/or chemical processes. Lignin is a three dimensional polymer that binds the cellulosic fibers together and with its removal from the raw material the cellulosic fibers are freed to act independently or for further processing (*e.g.*, into paper, craft board, etc.). Importantly, pulp is a hydrophilic material that is highly flexible (*i.e.*, has a low Young's modulus) and is available in a variety of fiber lengths and diameters. However, other hydrophilic fiber materials having the dimensions and material properties that allow their use in a wide range of fracture widths may be used in one or more embodiments.

[0029] In one or more embodiments, the hydrophilic fiber used may have a length with a lower limit of any of 50 microns, 100 microns, 200 microns, 250 microns, 325 microns, 400 microns, or 500 microns, with an upper limit of any of 1.5 millimeters, 2 millimeters, 3 millimeters, 5 millimeters, 6 millimeters, 8 millimeters, or 10 millimeters, where any lower limit can be used in combination with any upper limit. In one or more embodiments, a hydrophilic fiber sample may be further fractionated to achieve a more narrow length distribution within the ranges listed above. In one or more embodiments, the width (*e.g.*, dimension opposite the length) of the hydrophilic fibers may be from about 10 microns to 50 microns, or from about 15 microns to 45 microns, or from about 20 microns to 40 microns. In one or more embodiments, the

aspect ratio (length to width) of the hydrophilic fibers used in fracturing fluids of the present disclosure may be from about 5 to 1000, or from about 6.5 to 700, or from about 8 to 500, or from about 10 to 300.

[0030] The hydrophilic fibers of the present disclosure are more elastic and/or flexible than a comparably sized synthetic fiber. Without being bound by theory, the increased elasticity and/or flexibility of the hydrophilic fiber is believed to reduce the amount of bridging that occurs at the mouth/opening of fractures smaller than the hydrophilic fibers attempting to penetrate therein, thereby reducing the screening out of the hydrophilic fibers and facilitating their penetration into smaller fractures.

[0031] In one or more embodiments, the amount of hydrophilic fibers used in a fracturing fluid may be from about 0.012 to about 1.2 wt%, from about 0.06 wt% to about 0.9 wt%, from about 0.12 wt% to about 0.6 wt%, from about 0.18 wt% to about 0.48 wt% and from about 0.24 wt% to about 0.36 wt%.

[0032] The amount used may depend on the width of the fractures that are to be penetrated by the fracturing fluid. For example, in some embodiments the amount of hydrophilic fibers needed to effectively transport and place proppant within smaller width fractures may be less than that which is needed in larger width fractures due to the proppant size for smaller fractures being correspondingly smaller and the volume of smaller fractures being smaller.

[0033] In one or more embodiments, combinations of fibers (e.g., synthetic and hydrophilic and/or different types of hydrophilic fibers) may be used. For example, simply using one type or size of fiber for all fracture geometries may not achieve an optimized proppant transport and placement profile. For example, there is commonly a fracture width gradient within a formation, with the fracture width tending to be smaller the farther the fracture is from the wellbore. In these instances, some fibers may be too big to penetrate the smaller fractures and therefore cause bridging and/or plugging at the fracture opening/mouth. Conversely, some fibers may be too small to be able to anchor properly within larger fractures and suspend proppant therein.

[0034] WATER SOLUBLE POLYMER

[0035] As discussed above, the well treatment composition may further include a water soluble polymer, such as, for example, a polysaccharide, a polyelectrolyte or combinations thereof. Specific examples of polysaccharides include substituted galactomannans, such as guar gums, high-molecular weight polysaccharides composed of mannose and galactose sugars, or guar derivatives such as hydroxypropyl guar (HPG), carboxymethylhydroxypropyl guar (CMHPG) and carboxymethyl guar (CMG), hydrophobically modified guar, guar-containing compounds, cellulose derivatives such as hydroxyethylcellulose (HEC) or hydroxypropylcellulose (HPC), carboxymethylhydroxyethylcellulose (CMHEC) and carboxymethylcellulose (CMC), and synthetic polymers. Specific examples of polyelectrolytes include polyacrylamides, partially hydrolyzed polyacrylamides, partially hydrolyzed polymethacrylamide, sodium alginate, chitosan. Specific examples of polyelectrolyte polymers are described in U.S. Patent Application Pub. Nos. 2013/0056213 and 2013/0048283, the disclosures of which are incorporated by reference herein in their entirety.

[0036] Additional examples of water soluble polymer include acrylic acid-acrylamide copolymers, acrylic acid-methacrylamide copolymers, polyvinyl alcohols, polyalkyleneoxides, other galactomannans, heteropolysaccharides obtained by the fermentation of starch-derived sugar and their ammonium and alkali metal salts thereof. Suitable examples of biopolymers include gellan, κ -carrageenan, gelatin, agar, agarose, maltodextrin, and combinations thereof. The treatment composition may include any combination of the specific water soluble polymers described above.

[0037] The water soluble polymer may be present in an amount of from about 0.0012 to about 0.24 weight percent, 0.006 to about 0.12 weight percent, 0.012 to about 0.096 weight percent, 0.018 to about 0.06 weight percent, 0.024 to about 0.06 weight percent and from about 0.036 to about 0.048. The present inventors believe that a specific concentration of the water soluble polymer enhances the dispersion of the hydrophilic fiber when mixed together in an aqueous medium. Specifically, without wishing to be bound to a particular theory, the inventors believe that the water soluble polymer has an

affinity to the cellulose fiber and will absorb onto the surface of the fiber. This adhesion creates an increased steric repulsion between cellulose fibers due to the polymer covered surfaces, or an electrostatic repulsion based on the ionic nature of the water soluble polymer. The repulsion between cellulose surfaces increases the distance between the fibers which, in turn, reduces the friction between fibers and can more easily move past one another in flow. This phenomenon will help avoid or reduce creation of flocculates and enhance fiber dispersion.

[0038] In embodiments, the water soluble polymers may be functionalized to induce hydrophilic functionalization, such as, for example, carboxylic acid groups, thiol groups, paraffin groups, silane groups, sulfuric acid groups, acetoacetylate groups, polyethylene oxide groups, and/or quaternary amine groups.

[0039] The well treatment composition may further include a salt, such as, for example, potassium chloride, calcium chloride, sodium chloride, and mixtures thereof. The salt may be present in an amount of from about 0.1 wt% to about 5 wt% , such as, for example, from about 0.5 wt% to about 3 wt% and from about 1 wt.% to about 2 wt%. If present, the salt may further reduce the amount of the water soluble polymer in the well treatment composition. Additionally, the presence of salt in the mixture of polymer and cellulose fibers may increase affinity of the polymer to the fiber, creating an irreversible absorption of the polymer onto the fiber surface. The repulsion between cellulose surfaces increases the distance between the fibers which, in turn, reduces the friction between fibers and can more easily move past one another in flow. This phenomenon will help avoid or reduce creation of flocculates and enhance fiber dispersion.

[0040] As discussed above, the treatment fluid carrying the one or more polymers may be any well treatment fluid, such as a fluid loss control pill, a water control treatment fluid, a scale inhibition treatment fluid, a fracturing fluid, a gravel packing fluid, a drilling fluid, and a drill-in fluid. The carrier solvent for the treatment fluid may be a pure solvent or a mixture. Suitable solvents for use with the methods of the present disclosure, such as for forming the treatment fluids disclosed herein, may be aqueous or organic based. Aqueous solvents may include at least one of fresh water, sea water,

brine, mixtures of water and water-soluble organic compounds and mixtures thereof. Organic solvents may include any organic solvent that is able to dissolve or suspend the various components, such as the chemical entities and/or components of the treatment fluid.

[0041] While the treatment fluids of the present disclosure are described herein as comprising the above-mentioned components, it should be understood that the fluids of the present disclosure may optionally comprise other chemically different materials. In embodiments, the fluid may further comprise stabilizing agents, surfactants, diverting agents, or other additives. Additionally, the treatment fluid may comprise a mixture various other crosslinking agents, and/or other additives, such as fibers or fillers, provided that the other components chosen for the mixture are compatible with the intended use of forming a polymeric structure. In embodiments, the treatment fluid of the present disclosure may further comprise one or more components such as, for example, a gel breaker, a buffer, a proppant, a clay stabilizer, a gel stabilizer, a chelating agent, an oxygen scavenger and a bactericide. Furthermore, the treatment fluid or treatment fluid may include buffers, pH control agents, and various other additives added to promote the stability or the functionality of the fluid. The treatment fluid or treatment fluid may be based on an aqueous or non-aqueous solution. The components of the treatment fluid or treatment fluid may be selected such that they may or may not react with the subterranean formation that is to be treated.

[0042] In this regard, the treatment fluid may include components independently selected from any solids, liquids, gases, and combinations thereof, such as slurries, gas-saturated or non-gas-saturated liquids, mixtures of two or more miscible or immiscible liquids, and the like, as long as such additional components allow for the formation of a polymeric structure. For example, the fluid or treatment fluid may comprise organic chemicals, inorganic chemicals, and any combinations thereof. Organic chemicals may be monomeric, oligomeric, polymeric, crosslinked, and combinations, while polymers may be thermoplastic, thermosetting, moisture setting, elastomeric, and the like. Inorganic chemicals may be metals, alkaline and alkaline earth chemicals, minerals, and the like. Fibrous materials may also be included in the fluid or treatment fluid. Suitable

fibrous materials may be woven or nonwoven, and may be comprised of organic fibers, inorganic fibers, mixtures thereof and combinations thereof.

[0043] Surfactants can be added to promote dispersion or emulsification of components of the fluid, or to provide foaming of the crosslinked component upon its formation downhole. Suitable surfactants include alkyl polyethylene oxide sulfates, alkyl alkylolamine sulfates, modified ether alcohol sulfate sodium salts, or sodium lauryl sulfate, among others. Any surfactant which aids the dispersion and/or stabilization of a gas component in the fluid to form an energized fluid can be used. Viscoelastic surfactants, such as those described in U.S. 6,703,352, U.S. 6,239,183, U.S. 6,506,710, U.S. 7,303,018 and US 6,482,866, each of which are incorporated by reference herein in their entirety, are also suitable for use in fluids in some embodiments. Examples of suitable surfactants also include, but are not limited to, amphoteric surfactants or zwitterionic surfactants. Alkyl betaines, alkyl amido betaines, alkyl imidazolines, alkyl amine oxides and alkyl quaternary ammonium carboxylates are some examples of zwitterionic surfactants. An example of a useful surfactant is the amphoteric alkyl amine contained in the surfactant solution AQUAT 944 (available from Baker Petrolite of Sugar Land, Texas). A surfactant may be added to the fluid in an amount in the range of about 0.01 wt. % to about 10 wt. %, such as about 0.1 wt. % to about 2 wt. % based upon total weight of the treatment fluid.

[0044] Charge screening surfactants may be employed. In some embodiments, the anionic surfactants such as alkyl carboxylates, alkyl ether carboxylates, alkyl sulfates, alkyl ether sulfates, alkyl sulfonates, α -olefin sulfonates, alkyl ether sulfates, alkyl phosphates and alkyl ether phosphates may be used. Anionic surfactants have a negatively charged moiety and a hydrophobic or aliphatic tail, and can be used to charge screen cationic polymers. Examples of suitable ionic surfactants also include, but are not limited to, cationic surfactants such as alkyl amines, alkyl diamines, alkyl ether amines, alkyl quaternary ammonium, dialkyl quaternary ammonium and ester quaternary ammonium compounds. Cationic surfactants have a positively charged moiety and a hydrophobic or aliphatic tail, and can be used to charge screen anionic polymers such as CMHPG. In the same manner, a charged surfactant can also be

employed to form polymer-surfactant complexes as a method for generating consolidated structures.

[0045] In other embodiments, the surfactant is a blend of two or more of the surfactants described above, or a blend of any of the surfactant or surfactants described above with one or more nonionic surfactants. Examples of suitable nonionic surfactants include, but are not limited to, alkyl alcohol ethoxylates, alkyl phenol ethoxylates, alkyl acid ethoxylates, alkyl amine ethoxylates, sorbitan alkanoates and ethoxylated sorbitan alkanoates. Any effective amount of surfactant or blend of surfactants may be used in aqueous energized fluids.

[0046] Friction reducers may also be incorporated in any fluid embodiment. Any suitable friction reducer polymer, such as polyacrylamide and copolymers, partially hydrolyzed polyacrylamide, poly(2-acrylamido-2-methyl—1-propane sulfonic acid) (polyAMPS), and polyethylene oxide may be used. Commercial drag reducing chemicals such as those sold by Conoco Inc. under the trademark "CDR" as described in US 3,692,676 or drag reducers such as those sold by Chemlink designated under the trademarks FLO1003, FLO1004, FLO1005 and FLO1008 have also been found to be effective. These polymeric species added as friction reducers or viscosity index improvers may also act as excellent fluid loss additives reducing or even eliminating the use of conventional fluid loss additives. Latex resins or polymer emulsions may be incorporated as fluid loss additives. Shear recovery agents may also be used in embodiments.

[0047] Embodiments may also include proppant particles that are substantially insoluble in the fluids of the formation. Proppant particles carried by the treatment fluid remain in the fracture created, thus propping open the fracture when the fracturing pressure is released and the well is put into production. Suitable proppant materials include, but are not limited to, sand, walnut shells, sintered bauxite, glass beads, ceramic materials, naturally occurring materials, or similar materials. Mixtures of proppants can be used as well. If sand is used, it may be from about 20 to about 100 U.S. Standard Mesh in size. With synthetic proppants, mesh sizes about 8 or greater may be used. Naturally

occurring materials may be underived and/or unprocessed naturally occurring materials, as well as materials based on naturally occurring materials that have been processed and/or derived. Suitable examples of naturally occurring particulate materials for use as proppants include: ground or crushed shells of nuts such as walnut, coconut, pecan, almond, ivory nut, brazil nut, etc.; ground or crushed seed shells (including fruit pits) of seeds of fruits such as plum, olive, peach, cherry, apricot, etc.; ground or crushed seed shells of other plants such as maize (e.g., corn cobs or corn kernels), etc.; processed wood materials such as those derived from woods such as oak, hickory, walnut, poplar, mahogany, etc., including such woods that have been processed by grinding, chipping, or other form of particulation, processing, etc.

[0048] The concentration of proppant in the fluid can be any concentration known in the art. For example, the concentration of proppant in the fluid may be in the range of from about 0.03 to about 3 kilograms of proppant added per liter of liquid phase. Also, any of the proppant particles can further be coated with a resin to potentially improve the strength, clustering ability, and flow back properties of the proppant.

[0049] A fiber component, in addition to the hydrophilic fiber discussed above, may be included in the fluids to achieve a variety of properties including improving particle suspension, and particle transport capabilities, and gas phase stability. The fiber component may also be hydrophilic or hydrophobic in nature. The fiber component can be any fibrous material, such as, for example, natural organic fibers, comminuted plant materials, synthetic polymer fibers (by non-limiting example polyester, polyaramide, polyamide, novoloid or a novoloid-type polymer), fibrillated synthetic organic fibers, ceramic fibers, inorganic fibers, metal fibers, metal filaments, carbon fibers, glass fibers, ceramic fibers, natural polymer fibers, and any mixtures thereof. Particularly useful fibers are polyester fibers coated to be highly hydrophilic, such as, but not limited to, DACRON® polyethylene terephthalate (PET) fibers available from Invista Corp. Wichita, KS, USA, 67220. Other examples of useful fiber components include, but are not limited to, polylactic acid polyester fibers, polyglycolic acid polyester fibers, polyvinyl alcohol fibers, and the like. The fiber component may present in the amounts described above for the hydrophilic fiber.

[0050] Embodiments may further use fluids containing other additives and chemicals that are known to be commonly used in oilfield applications by those skilled in the art. These include materials such as surfactants in addition to those mentioned hereinabove, breaker aids in addition to those mentioned hereinabove, oxygen scavengers, alcohol stabilizers, scale inhibitors, corrosion inhibitors, fluid-loss additives, bactericides and biocides such as 2,2-dibromo-3-nitrilopropionamine or glutaraldehyde, and the like. Also, they may include a co-surfactant to optimize viscosity or to minimize the formation of stable emulsions that contain components of crude oil.

[0051] In one or more embodiments, the fluid system may include a thickener selected from natural polymers including guar (phytogenous polysaccharide) and guar derivatives (e.g., hydroxypropyl guar and carboxymethylhydroxypropyl guar) and synthetic polymers including polyacrylamide copolymers. Additionally, viscoelastic surfactants that form elongated micelles are another class of non-polymeric viscosifiers that may be added to the fluid in addition to or independently from the polymeric thickeners. Other polymers and other materials, such as xanthan, scleroglucan, cellulose derivatives, polyacrylamide and polyacrylate polymers and copolymers, viscoelastic surfactants, and the like, can be used also as thickeners. For example, water with guar represents a linear gel with a viscosity that increases with polymer concentration.

[0052] In hydraulic and acid fracturing, a first fluid called the pad may be injected into the formation to initiate and propagate the fracture. This is followed by a second fluid that contains a proppant to keep the fracture open after the pumping pressure is released. The hydrophilic fibers of the present disclosure may be included in either fluid, and in particular embodiments, may be included in the second fluid to help suspend proppants.

[0053] However, it is envisioned that the hydrophilic fibers may be used for carrying out a variety of subterranean treatments/wellbore operations including, but not limited to, drilling operations, diverting treatments, gravel packing, zonal isolation, or downhole delivery. Such operations are known to persons skilled in the art and involve pumping a

wellbore fluid into a wellbore through an earthen formation and performing at least one wellbore operation while the wellbore fluid is in the wellbore. Depending on the type of operation being performed, the size of the fibers selected may vary, *i.e.*, to form a plug in a diversion, longer fibers (relative to a fracture width) may be selected.

[0054] The technique that was used to measure changes in a fluid continuum, including formation of agglomerates or existing flocculates. See Example 3. The method begins with using a rheometer with low sensitivity in torque measurements (at least 0.05nN-m torque resolution). The rheometer is used with a couette geometry or concentric cylinder geometry, where the inner wall rotates to induce a shear in the gap. Initially, the prepared fluid is placed in said gap (in the annular space between the concentric cylinders). Then, the experiment is set for the inner cylinder to rotate at a constant speed while measuring the torque exerted to maintain such speed.

[0055] If a fluid inside the gap contains particles that agglomerate over time or under flow, the torque reading will increase once the agglomerate size exceeds the gap of the annulus between the cylinders. If no agglomeration occurs in the fluid, the torque is to remain constant though the duration of the test. On the other hand, if an agglomerate is formed and then dissipated with time or shear then a momentary increase in torque is observed followed by a sharp decrease.

[0056] The foregoing is further illustrated by reference to the following examples, which are presented for purposes of illustration and are not intended to limit the scope of the present disclosure.

[0057] **EXAMPLES**

[0058] **Example 1**

[0059] Cellulose fibers, especially the long pulp fibers, do not disperse well in water without any dispersing agent. Fibers can be separated by high shear mixing but reassemble again once shearing has stopped.

[0060] Example 1a (comparative) was prepared by first mixing the 0.48 wt% pulp fibers in tap water with Waring blender at 3000 rpm for 10 min; water soluble polymers, such

as CMC have to be pre-hydrated with a Waring blender at 3000 rpm for 10 min before fibers are added. Then 10 mL of the mixed fluid are taken and poured into a petri dish for optical microscope study.

[0061] Example 1b and Example 1c were prepared in the exact same manner as Example 1a except that 0.012 wt% of CMC (Example 1b) and 0.048 wt% of CMC (Example 1c) was added to the treatment fluid. Microscopic images of Examples 1a-1c were taken using a Leica Model MSV266 microscope.

[0062] Figures 1a-c depict optical microscope images of (a) 0.48 wt% pulp fibers without CMC; (b) 0.48 wt% pulp fibers with 0.012 wt% CMC; (c) 0.48 wt% pulp fibers with 0.048 wt% CMC.

[0063] As depicted, **Error! Reference source not found.**(a) shows a treatment fluid that looks cloudy with fibers forming aggregates. However, as shown in Figures 1(b) and 1(c), the addition of CMC significantly improved the dispersion where the sample was clear and contained no fiber aggregates.

[0064] **Example 2:**

[0065] The effect of CMC on pulp fiber dispersion was further validated by conducting a bridging test. The bridging test was performed using slots of 16 mm in length, and 1 mm in width. The bridging test consists of flowing a liquid mixture through the slot at a controlled flow rate. The rate of fluid injection was varied from 10 to 800 mL/min to determine the bridging and non-bridging rate. The rate of flow was converted to linear velocity using the geometrical parameters of each slot (width and length). The bridging ability of the fluid was determined by monitoring pressure responses and observing if fiber agglomerates blocked the slot. Minor change in pressure (ΔP below 10 psi) with no fiber at the entrance or inside the slot was considered a non-bridging result. Pressure change response (ΔP) above 10 psi during the test and/or visual formation of fiber plug was considered a bridging phenomenon.

[0066] First, a benchmark test (Example 2a – comparative) was run first without CMC (Figures 2a-2b) and another test (Example 2b) using CMC (Figures 2c-2d). Example 2a

was prepared by combining 0.48 wt% pulp fibers, 0.04 wt% proprietary polymer blend and 0.14 wt% choline chloride.

[0067] Example 2b was prepared by hydrating 0.048 wt% of CMC in a Waring blender for 20 minutes at 3000 rpm along with 0.14 wt% choline chloride and 0.48 wt% of pulp fibers. This solution was mixed for 5 additional minutes, and finally 0.04 wt% proprietary polymer blend was added and the resulting solution was mixed for 5 additional minutes. Figures 1a-2d shows pictures of the slot after both bridging tests were conducted.

[0068] Figures 1a-d indicate bridging test results of 0.48 wt% pulp fibers in 1mm slot with and without addition of 0.048 wt% CMC.

[0069] As shown in Figures 2a-2b, the minimum non-bridging flow velocity observed for Example 2a (having no CMC) was 73 cm/s (Figures 1(b)). Any flow rate below the 73 cm/s threshold illustrated in Figure 2(b) caused the fibers to bridge such as 68 cm/s (Figures 1(a)). With 0.048 wt% CMC added, the non-bridging flow velocity threshold was reduced to 47 cm/s (Figure 2d); a significant improvement to decrease the tendency of bridging.

[0070] **Example 3:**

[0071] In this example the base fluid was composed of 0.012 wt% CMC, the polymer was hydrated in water for 20 minutes using a Waring blender at 3000 rpm. A quantity of 0.48 wt% of cellulose fibers was added to 23 mL of the previously hydrated CMC. The combination was then stirred with a hand-held mixer at high speed for 30 seconds. A rheometer with couette geometry was used to measure changes in torque of the fluid over a period of 30 seconds, at constant angular velocity. The results are shown in Figures 3a and 3b.

[0072] Figures 3a-b indicate experimental data using a rheometer with couette geometry to measure torque changes of the fluid over time at constant angular velocity. The CMC was fully hydrated before mixing with cellulose fibers, in two samples: 0.048 wt% CMC and 0.012 wt% CMC.

[0073] a-3b shows a comparison of average torque readings over time, at every constant velocity measured. Figure 3b is a ballooned version of Figure 3a, having a reduced y-axis plot to better illustrate the torque. Figures 3a-3b each indicate a comparison between torque readings of cellulose fibers dispersed in hydrated CMC (at 0.012 wt% and 0.048 wt% concentration), and cellulose fibers dispersed in water (no CMC added). The variability in the torque measurements for cellulose fibers indicate the presence of flocculates or aggregates forming and dissipating as they flow in accordance to the velocity of the bob. On the other hand, when the cellulose fibers are dispersed in CMC there is no observed variability in the torque indicating no formation of flocculates. See Figure 3b.

[0074] **Example 4:**

[0075] For this example, the torque measurement method described in Example 3 was used. This example is different from Example 3 in regards the mixing procedure of the cellulose fiber and the CMC. A Waring blender was used, where 0.48 wt% of cellulose fiber and 0.012 wt% of CMC were added at the same time to 100 mL of water. The components were mixed at 3000 rpm for 15 minutes, where the CMC was allowed to hydrate in the presence of the fibers. The results are shown in Figures 4a and 4b.

[0076] Figure 2a-4b depict experimental data using a rheometer with couette geometry to measure torque changes of the fluid over time at constant angular velocity. The cellulose fibers and CMC were mixed simultaneously.

[0077] In Figure 2 4a-4b, the torque measurements indicate less aggregation of 0.48 wt% fibers in CMC as a comparison to 0.48 wt% cellulose fibers without CMC, demonstrating that the method of mixing does not affect fiber dispersion.

[0078] **Example 5:**

[0079] Example 5a (comparative) was prepared by first mixing the 0.48 wt% pulp fibers with Waring blender at 3000 rpm for 10 min. Then 10 mL of the mixed fluid are taken and poured into a petri dish for optical microscope study.

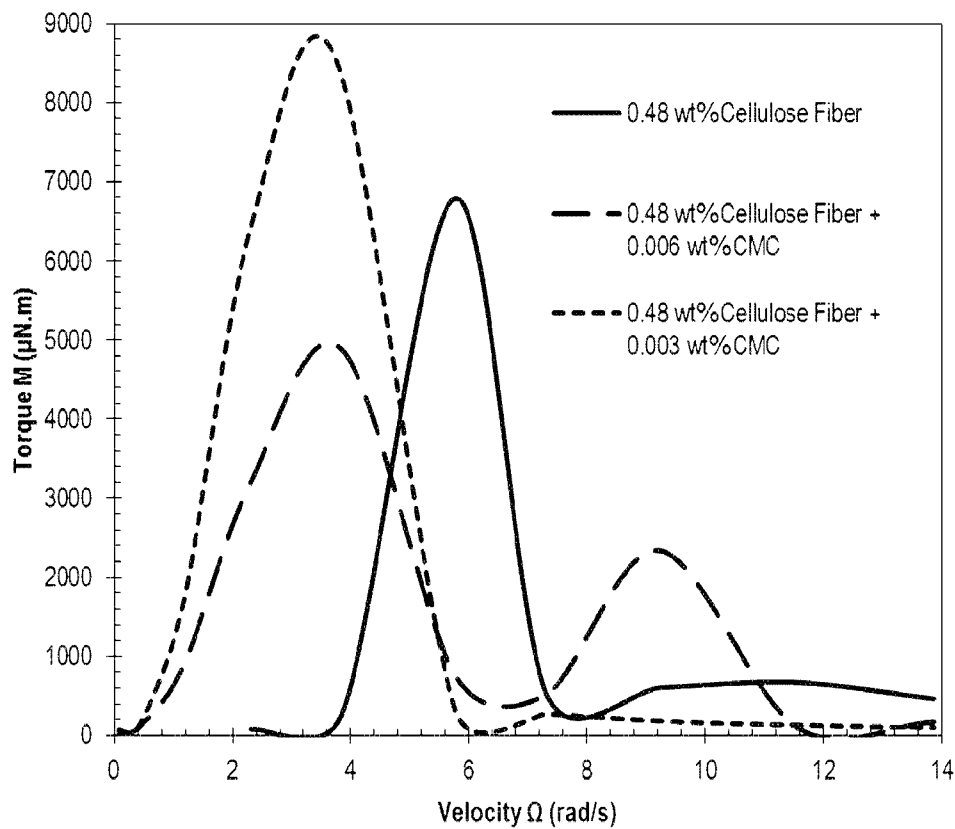
[0080] Example 1b and Example 1c were prepared in the exact same manner as Example 1a except that 0.032 wt% of polyacrylamide (Example 5b) and 0.06 wt% of guar (Example 5c) was added to the treatment fluid. Microscopic images of Examples 5a-5c were taken using a Leica Model MSV266 microscope, these images illustrated in Figures 5a-5c.

[0081] Figure 5 depicts optical microscope images of (a) 0.48 wt% fiber without additive; (b) 0.48 wt% fiber with 0.032 wt% polyacrylamide; (c) 0.48 wt% fiber with 0.06 wt% guar.

[0082] As shown, Example 5b (containing 0.032 wt% polyacrylamide) shows an improved dispersion as compared to Example 5a (see Figures 5a-5b). The same conclusion can be seen from Example 5c.

[0083] **Example 6**

[0084] This example was prepared using the same method of mixing the fluid and the measuring torque as described in Example 3. However, in Example 6, lower concentrations of CMC were added to a suspension of 0.48 wt% cellulose fiber. Two separate fluids were prepared, one with 0.006 wt% CMC and the other with 0.003 wt% CMC concentrations, both with 0.48 wt% of cellulose fiber. As shown in **Error! Reference source not found.**, there is an increase in torque measurements at 0.006 wt% and 0.003 wt% CMC. Similar in magnitude to the fluid measured in Example 3 without any CMC added. The data high torque measurement indicates the presence of fiber flocs in the fluids, which means that the lower concentrations of CMC do not help in fiber dispersion, below 0.012 wt%. However, addition of salt to the fluid may aid in fiber dispersion at lower concentrations of CMC.



[0085] Figure 6 depicts experimental data using a TA DHR-3 rheometer with couette geometry to measure torque changes of the fluid over time at constant angular velocity. The CMC was fully hydrated before mixing with cellulose fibers, in two samples: 0.006 wt% CMC and 0.003 wt% CMC.

[0086] Although only a few example embodiments have been described in detail above, those skilled in the art will readily appreciate that many modifications are possible in the example embodiments without materially departing from this invention. Accordingly, all such modifications are intended to be included within the scope of this disclosure as defined in the following claims.

CLAIMS

What is claimed:

1. A treatment fluid comprising:
 - an aqueous base fluid;
 - a proppant;
 - a water soluble polymer; and
 - hydrophilic fibers having a length of about 100 microns to 10 millimeters.
2. The treatment fluid of claim 1, wherein the hydrophilic fibers comprise pulp cellulose fibers.
3. The treatment fluid of claim 1, wherein the amount of water soluble polymers used in the fracturing fluid is from about 0.012 wt% to 0.12 wt%.
4. The treatment fluid of claim 1, wherein the water soluble polymers comprise polyelectrolytes or non-charged polymers.
5. The treatment fluid claim 1, wherein the water soluble polymer is selected from the group consisting of carboxymethyl cellulose (CMC), chitosan, hydroxyethyl cellulose (HEC), guar, carboxymethyl hydroxypropyl guar (CMHPG), polyacrylamide, alginate, polyvinyl alcohol, poly (maleic acid), polyvinyl amine, and combinations thereof.
6. The treatment fluid of claim 1, wherein the water soluble polymer is modified or functionalized.
7. A method of treating a subterranean formation, the method comprising:
 - forming a treatment fluid comprising:
 - an aqueous base fluid;

a proppant;
a water soluble polymer; and
hydrophilic fibers having a length of about 100 microns to 10 millimeters;
and
placing the treatment fluid in the subterranean formation.

8. The method of claim 7, wherein the hydrophilic fibers are pulp cellulose fibers.
9. The method of claim 7, wherein the amount of the water soluble polymer used in the fracturing fluid is from about 0.6 mg per gram of the hydrophilic fiber added to 120 mg per gram of the hydrophilic fiber added.
10. The method of claim 7, wherein the water soluble polymer comprises a polyelectrolyte or a non-charged polymer.
11. The method of claim 7, wherein the water soluble polymer is selected from the group consisting of carboxymethyl cellulose (CMC), chitosan, hydroxyethyl cellulose (HEC), guar, carboxymethyl hydroxypropyl guar (CMHPG), polyacrylamide, alginate, polyvinyl alcohol, poly (maleic acid), polyvinyl amine, and combinations thereof.

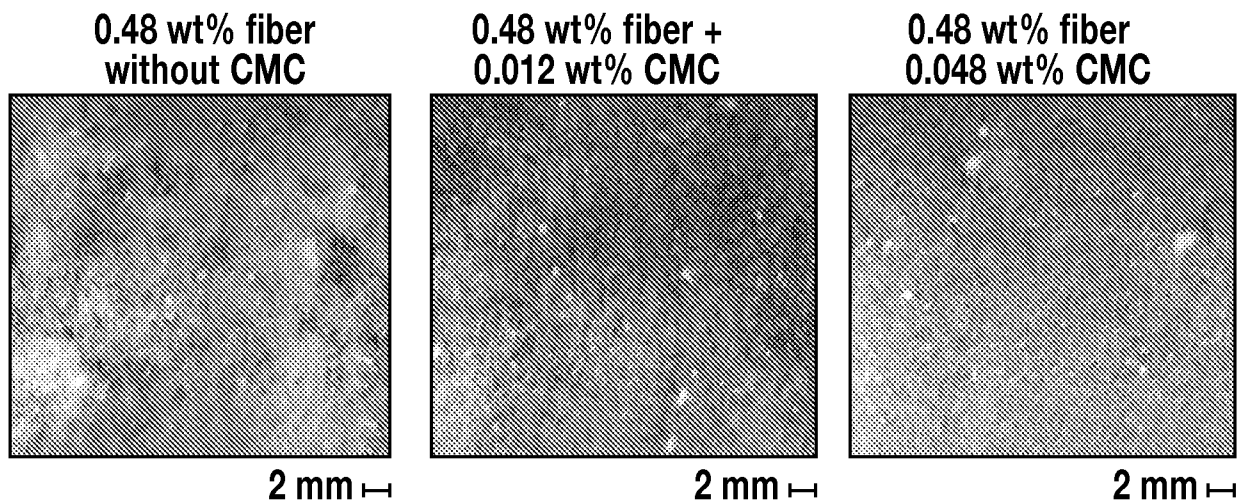
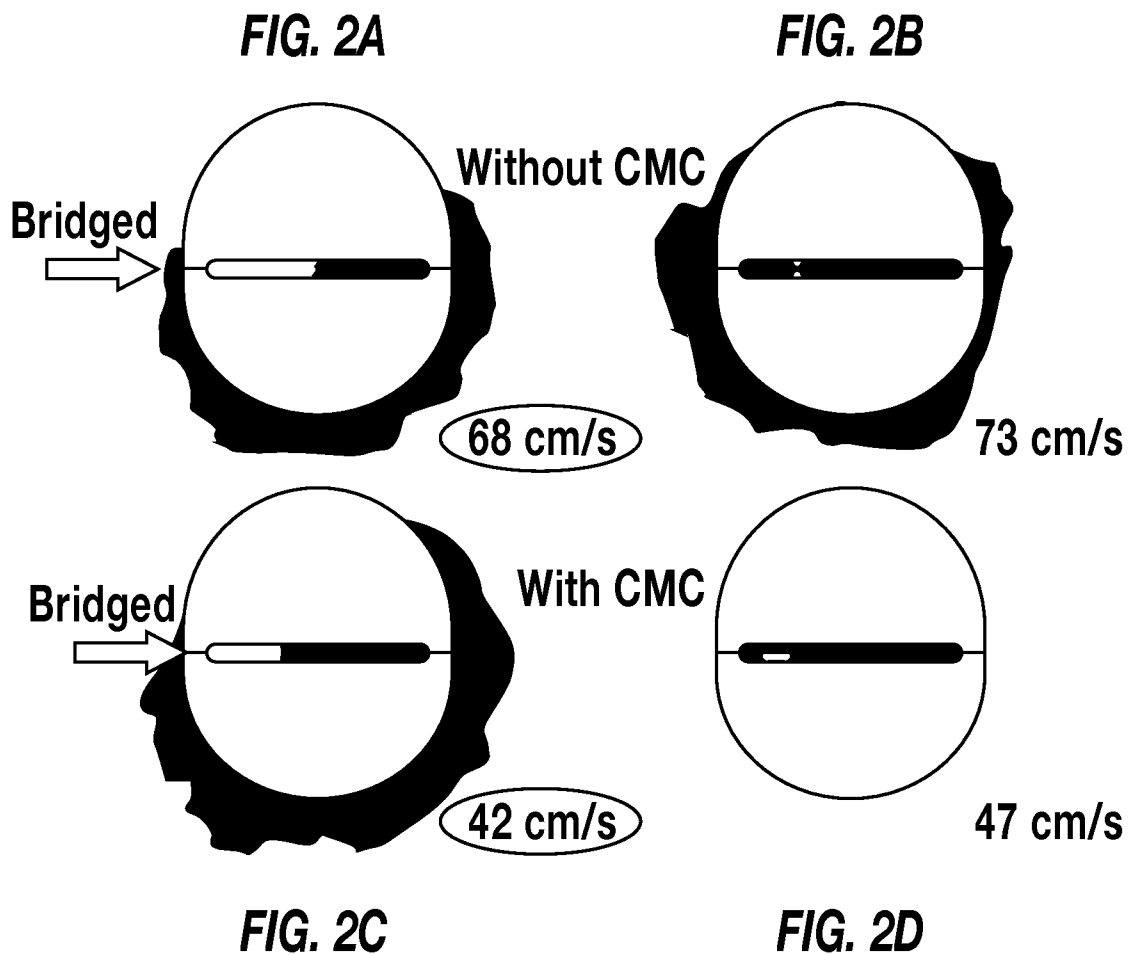
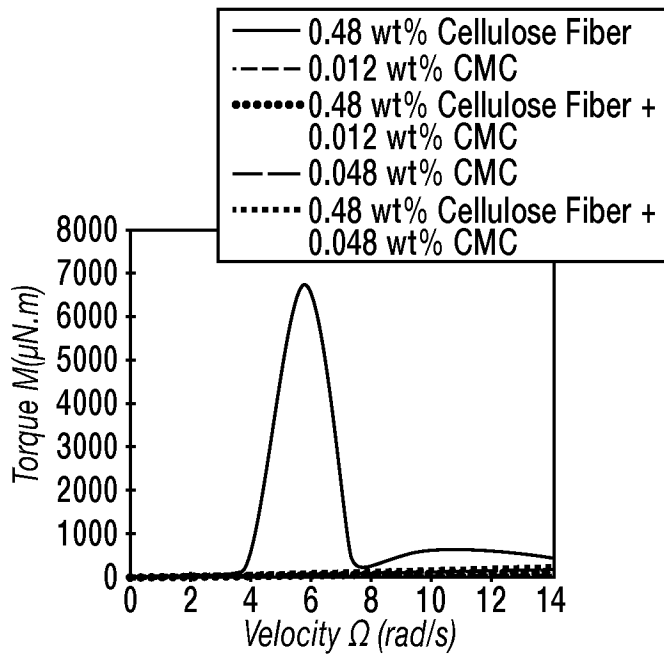
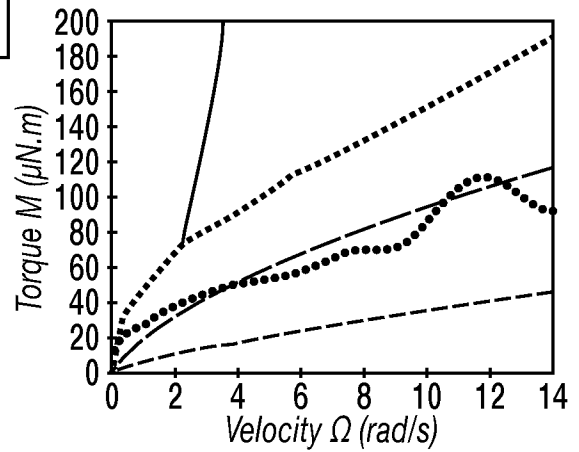
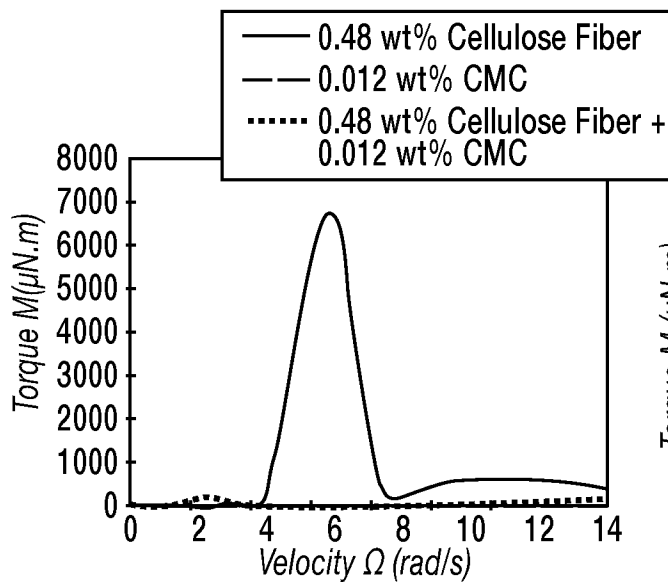
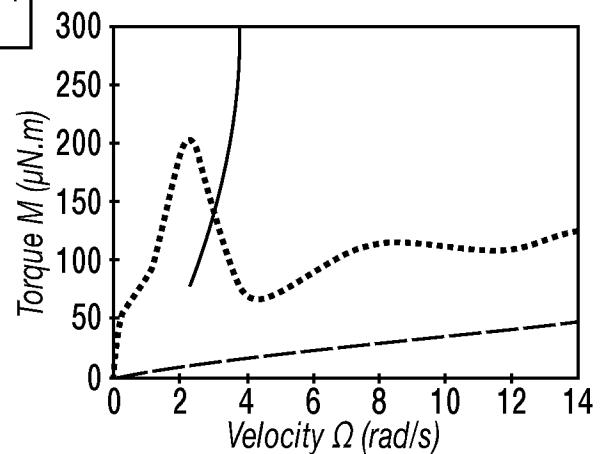
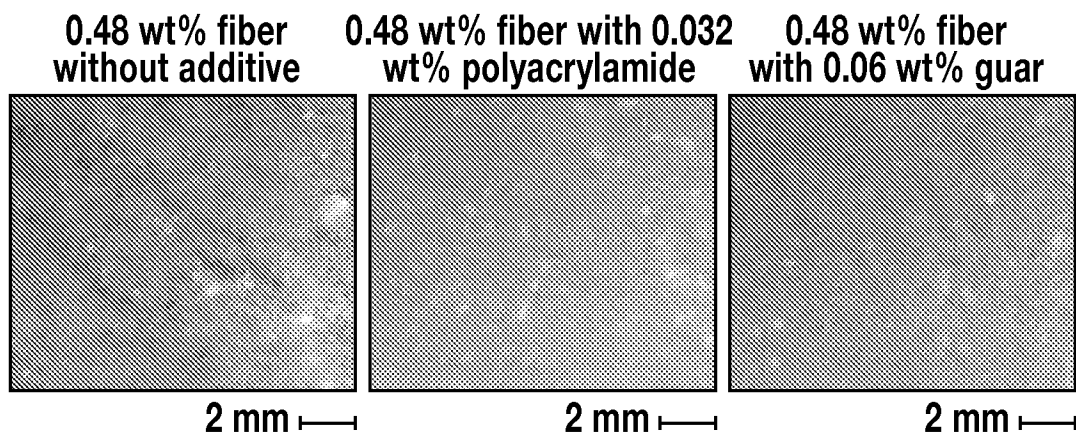


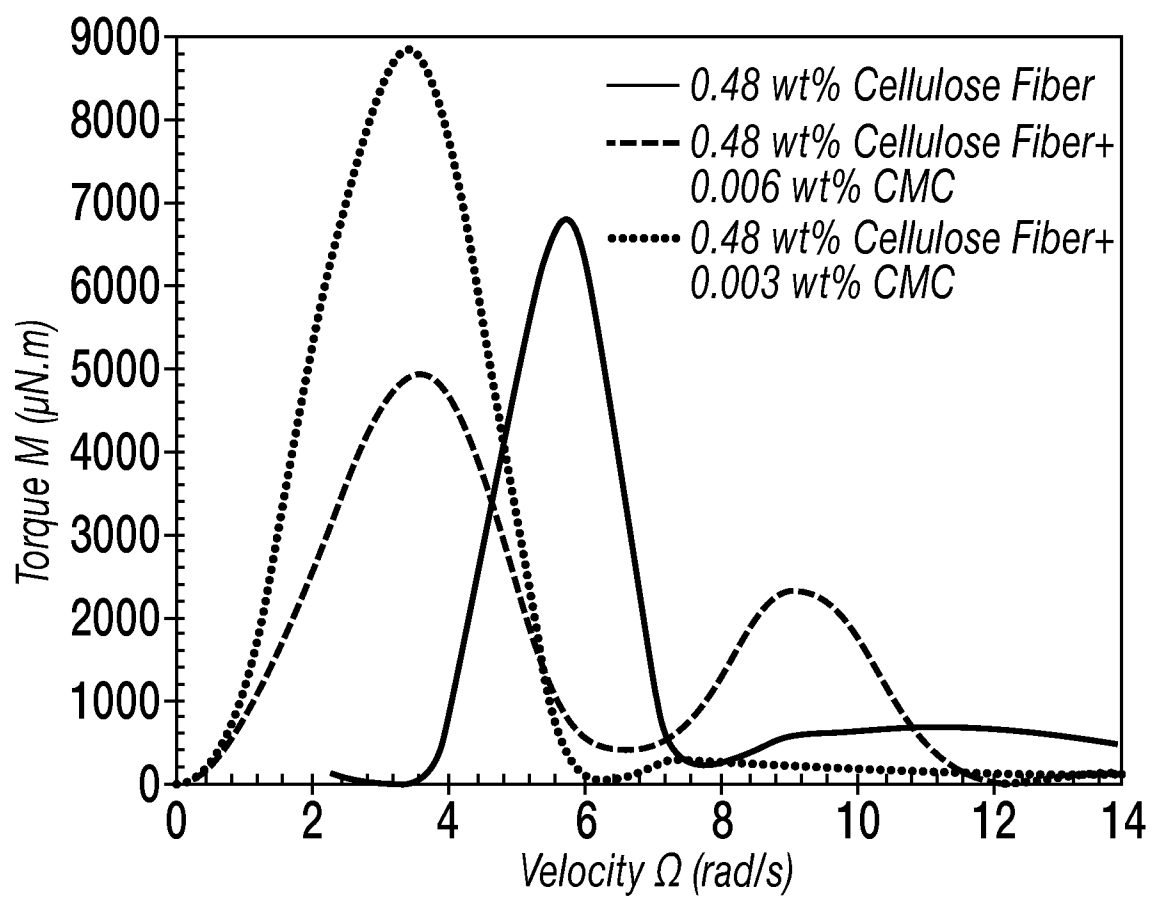
FIG. 1A

FIG. 1B

FIG. 1C



**FIG. 3A****FIG. 3B****FIG. 4A****FIG. 4B****FIG. 5A****FIG. 5B****FIG. 5C**

**FIG. 6**

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2017/056359**A. CLASSIFICATION OF SUBJECT MATTER****C09K 8/92(2006.01)i, C09K 8/80(2006.01)i, C09K 8/84(2006.01)i**

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C09K 8/92; E21B 43/22; E21B 43/26; C09K 8/90; C09K 3/00; C09K 8/10; C09K 8/80; C09K 8/84

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & Keywords: hydrophilic, fiber, pulp, cellulose, polysaccharide, proppant, fracturing

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6016871 A (BURTS, JR., BOYCE D.) 25 January 2000 See column 4, lines 29-35, 47-53; column 6, lines 30-38; column 8, lines 44-45; and claims 1, 3-4, 9.	1-11
X	WO 2016-060120 A1 (OJI HOLDINGS CORPORATION) 21 April 2016 See paragraphs [0018], [0025], [0061], [0101]-[0102], [0106], [0112]; and claims 1-2, 8-11.	1-11
A	WO 2016-002688 A1 (OJI HOLDINGS CORPORATION) 07 January 2016 See the whole document.	1-11
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PX	WO 2016-187490 A1 (SCHLUMBERGER TECHNOLOGY B.V.) 24 November 2016 See paragraphs [0041], [0051]-[0052]; and claims 1-2, 8, 12, 14, 16.	1-11



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

25 January 2018 (25.01.2018)

Date of mailing of the international search report

25 January 2018 (25.01.2018)

Name and mailing address of the ISA/KR

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2017/056359

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