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(54) Title: SEALING ELEMENT AND RELATED METHODS

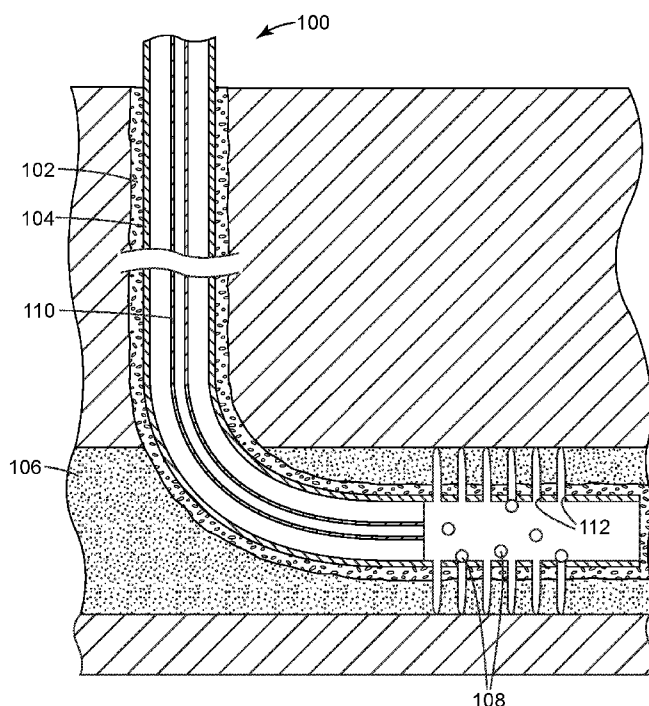


Fig. 1

(57) Abstract: Provided are sealing elements useful for isolating or diverting segments of a well in a hydraulic fracturing operation. These sealing elements resist the extreme temperatures and pressures encountered within a well, yet can be degraded or dissolved when no longer needed without use of hazardous acids or other chemicals. The sealing elements are made from a composite containing one or more resins of polylactic acid combined with a degradant that can be customized to provide facile degradation of the sealing element over a wide range of operative temperatures and pressures. These compositions may optionally include a swellant that causes the sealing element to expand after being seated against a well perforation or passageway to provide an enhanced seal.



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SEALING ELEMENT AND RELATED METHODS

Field

5 Provided are articles and methods related to sealing elements used in a subterranean well. More particularly, the sealing elements are useful for sealing at least a portion of the well for a hydraulic fracturing process.

Background

10 The oil and gas industry commonly uses a process known as hydraulic fracturing (or “fracking”) to recover oil or natural gas residing in subterranean formations deep within the earth. This typically involves pumping a fracturing fluid, generally water mixed with a proppant, such as sand, and one or more thickening agents, into the well at sufficient pressures to open up new fissures in the formation through which oil or gas can flow into the well.

15 It is common for wells to have perforations or passageways, each of which can be subjected to hydraulically-induced fracturing pressure. Since the initiation of new fractures in the formation generally requires greater pressure than that used to maintain existing fractures, so sealing elements (which include, for example, ball sealers or frac balls) can be used to obstruct at least some of the perforations or passageways to isolate some segments of the well to the fracturing fluid while diverting flow to others.

20 To close off one segment of a well from an adjacent segment, for example, an annular seat can be disposed in the well between the segments. The annular seat provides a constriction that is narrower than the diameter of the sealing element, which enables the sealing element to form a seal against the seat and prevent flow therethrough.

 Known sealing elements are generally spherical in shape and are made from a core of nylon, phenolic resin, or a metal such as aluminum. The core of the sealing element can optionally be covered with a polymer, such as a rubber, to protect the core from solvents and/or enhance their sealing ability.

 Once the sealing element has served its purpose, it is desirable for it to be removed from the sealing location to restore fluid flow into the segment of the well that was previously blocked. This is a significant engineering challenge. Prior approaches have used differences between the density of the sealing element and surrounding fluid in the well to either “sink” them to the bottom of the well or “float” them to the surface, but these tend to significantly complicate the well treatment process and/or hamper the ability to carry out further well operations. A problem with this approach is that these sealing elements can become permanently stuck within a wellbore passageway or perforation. Such sealing elements must then be milled out, which is both expensive and time consuming.

35 Another option is to degrade the sealing element by using a polymer capable of dissolving or degrading in aqueous environments. Such polymers include polyvinyl alcohol (“PVA”), polyvinyl acetate (“PVAC”), polyethylene oxide (“PEO”), polypropylene oxide (“PPO”), and polylactic acid (“PLA”). Commercially available sealing elements made from these polymers, however, have not

provided adequate toughness and strength under operating environments with the ability to degrade on demand and over a short period of time.

As a further option, it is possible to use metallic sealing elements that degrade based on galvanic corrosion in the presence of a suitable electrolyte. These materials have the advantage of high strength and relatively fast rates of dissolution. Their drawbacks include hazardous shipment requirements, use of inflexible materials, and high manufacturing cost.

Summary

The provided sealing elements and methods thereof are resistant to the extreme temperatures and pressures encountered deep within a well and yet can be degraded or dissolved in an environmentally safe manner when no longer needed. At depths that can reach 4500 meters or more, downhole components encounter not only high temperatures and pressures, but also become exposed to carbon dioxide, hydrogen sulfide, and acid compounds such as hydrogen chloride, that can result in premature erosion.

The provided sealing elements and methods use a composite containing one or more resins of polylactic acid combined with a degradant formulated to provide facile degradation of the sealing element over a wide range of operative temperatures and pressures. Optionally, these compositions further include a swellant that enables the sealing element to expand after being seated against a well perforation or passageway to provide an enhanced seal.

In a first aspect, a sealing element for sealing at least a portion of a well for a hydraulic fracturing process is provided. The sealing element is made from a composite comprising: an amorphous polylactic acid resin; and cellulose acetate propionate.

In a second aspect, a sealing element for sealing at least a portion of a well for a hydraulic fracturing process is provided, the sealing element made from a composite comprising: a polylactic acid resin; a swellant selected from modified starch, polyvinylpyrrolidone, and combinations thereof; and citric acid.

In a third aspect, a sealing element for sealing at least a portion of a well for a hydraulic fracturing process is provided, the sealing element made from a composite comprising: a polylactic acid resin; and a swellant comprising modified starch, wherein the composite is generally solid.

In a fourth aspect, a method of sealing at least a portion of a well for a hydraulic fracturing process comprising: placing one of the aforementioned sealing elements against a perforation or passageway within the well, the perforation or passageway having a smaller cross-section than the sealing element to restrict fluid communication between a first segment and a second segment of the well; and degrading the sealing element to restore the fluid communication between the first and second segments.

In a fifth aspect, a sealing element for sealing at least a portion of a well for a hydraulic fracturing process is provided, the sealing element made from a composite comprising: a polylactic acid resin; and a swellant comprising polyvinylpyrrolidone.

Brief Description of the Drawings

FIG. 1 is a side, cross-sectional view showing use of sealing elements in an exemplary subterranean well;

FIG. 2 is an enlarged side, cross-sectional view showing use of a sealing element in an exemplary well segment; and

FIG. 3 is a plot showing the change in mass of a sealing element over time at two different temperatures.

Repeated use of reference characters in the specification and drawings is intended to represent the same or analogous features or elements of the disclosure. It should be understood that numerous other modifications and embodiments can be devised by those skilled in the art, which fall within the scope and spirit of the principles of the disclosure.

The figures may not be drawn to scale.

DEFINITIONS

As used herein:

“compliant” refers to materials having an elastic modulus of less than about 2 GPa; “diverting agent” refers generally to an agent that functions to prevent, either temporarily or permanently, the flow of a fluid into a particular location by sealing off the location and causing the fluid to flow to a different location;

“treatment,” or “treating,” refers to any well or subterranean operation performed in conjunction with a desired function and/or for a desired purpose;

“fracturing fluid” refers generally to any fluid that may be used in a subterranean application in a hydraulic fracturing process;

“plasticizer” refers to a compound that reduces the glass transition temperature of a polymer when mixed therein;

“soluble” means capable of being at least partially dissolved upon exposure to a suitable solvent, such as well fluids, at conditions found in a subterranean formation;

“deformable” means capable of being permanently put out of shape; and “seal” means to occlude an opening by about 95% or more.

Detailed Description

An exemplary well is illustrated in FIG. 1 and herein referred to by the numeral 100. As shown, the well includes a wellbore 102 lined with its associated casing 104 penetrating a subterranean formation. The wellbore 102 extends into a particular zone of interest 106, such as a layer of hydrocarbon bearing formation. Optionally and as shown, the wellbore 102 descends vertically at first, but is then re-directed along a horizontal direction to extend parallel to the zone of interest 106.

The provided articles and methods are also useful in vertical wellbore configurations such as disclosed in U.S. Patent Publication No. 2013/0292123 (Murphree et al.).

One or more sealing elements 108 flow through the casing 104 into the zone of interest 106 while being pushed through by a workstring 110 into a plurality of perforations 112 disposed on the given segment of the wellbore casing 104.

5 The sealing elements 108 illustrated here are diverting materials. These diverting materials are monolithic, spherical solids (non-porous) and generally homogenous on a macroscopic scale (i.e., to the naked eye). These sealing elements 108 can be useful in diverting fluid from a portion of a subterranean formation during a stimulation operation. This is accomplished by allowing the sealing elements 108 described herein to form a seal against respective perforations 112 of the casing 104, as shown in FIG. 1, and act as a barrier to the flow of fracturing fluid into the perforations, thus redirecting the fracturing fluid
10 to unsealed perforations in the wellbore 102.

While spherical sealing elements 108 are depicted in FIG. 1, it is further understood that other shapes are also possible. Such shapes could include flake-like, elongated, and dart-shaped configurations such as described in U.S. Patent No. 8,231,947 (Vaidya et al.).

15 Additionally, in some cases, the perforations to be sealed by the sealing elements 108 includes naturally-occurring fissures in the subterranean formation.

FIG. 2 shows a well 200 according to a second exemplary embodiment showing a wellbore 202 lined with a casing 204 and separated into a first segment 216 and a second segment 218. The first and second segments 216, 218 are adjacent to each other and separated from each other by an annular seat 220. As shown, a sealing element 208 is seated against the annular seat 220, which has a circular
20 constriction 222. The constriction 222 has a diameter less than that of the sealing element 208, enabling the sealing element 208 to form a fluid tight seal against the annular seat 220 and prevent flow of fracturing fluids between the first and second segments 216, 218.

The size of the sealing element generally depends on the size of the perforation or passageway to be sealed and can range, for example, from diverting materials as small as 100 micrometers in diameter to
25 frac balls as large as 13 centimeters in diameter.

While not shown here, alternative embodiments use sealing elements that are granular—that is, sealing elements in the form of discrete, solid particles that are optionally part of an aqueous slurry composition. The aqueous slurry can be injected into a well to form a plug of a degradable material. A downhole operation can then be performed around the plug, and the plug later degraded for removal. The
30 discrete, solid particles can take any known form, such as pellets, flakes, fibers, and mixtures thereof. The size of the particles need not be restricted, and can have either a monomodal or multimodal particle size distribution. Further options and advantages associated with slurry-based degradable diverters are described elsewhere, for example in U.S. Patent No. 7,565,929 (Bustos et al.).

A given sealing element can be advantageously degraded to restore fluid communication between
35 the portions of the well previously isolated from each other. This can be actuated by exposing the sealing element to a fracturing fluid. The fracturing fluid is preferably an aqueous fluid. The aqueous fluid can be acidic or basic, but this need not be the case. For example, the provided sealing elements were observed to degrade in pure water at a temperature of 170°C and a pressure of approximately 0.8 MPa.

Actual pressures encountered in the subterranean formations where the sealing elements are located can be much higher; hydraulic fracturing is commonly conducted at hydrostatic pressures of over 100 megapascals (or 15,000 psi).

The period of time over which the sealing element is degraded is not particularly restricted. It is preferred that this period of time, however, be sufficiently short to avoid unnecessarily delays in well stimulation operations, yet sufficiently long to avoid unintended or premature degradation of the sealing element. In some instances, the degradation period required to obtain a given target mass loss can be at least 6 hours, at least 10 hours, at least 15 hours, at least 30 hours, at least 60 hours, at least 80 hours, at least 100 hours, or at least 120 hours. The aforementioned degradation period can be up to 170 hours, up to 150 hours, up to 125 hours, up to 100 hours, up to 80 hours, up to 65 hours, up to 50 hours, or up to 40 hours.

The target mass loss for a sealing element depends on the application and can be at least 0.5 percent, at least 1 percent, at least 5 percent, at least 10 percent, at least 30 percent, at least 45 percent, or at least 60 percent. The target mass loss can be up to 100 percent, up to 90 percent, up to 80 percent, up to 65 percent, up to 50 percent, up to 40 percent, or up to 35 percent.

The provided sealing elements are made from a composite containing a degradable composition. Provided degradable compositions include one or more polylactic acid resins and one or more functional fillers. Polylactic acid ("PLA," also referred to as poly(2-hydroxypropanoic acid)) is a biodegradable thermoplastic polyester that can be produced from renewable resources such as corn. Polylactic acid is known to be recycled to monomer by thermal depolymerization or hydrolysis.

The polylactic acid resin or resins of the sealing elements may be fully amorphous, semi-crystalline, or a blend of both. The microstructure of the polylactic acid resin depends on the stereopurity of its polymer backbone. Mixtures of stereoisomers L-PLA and D-PLA can be combined in various ratios to control the rate of crystallization and obtain specific grades based on their respective applications.

The polylactic acid resin preferably represents a continuous phase in the composite, although it need not be a majority phase. The polylactic acid resin can function as either a matrix material or binder capable of surrounding and binding together discrete, particulate fillers in the composite. The overall amount of polylactic acid resin in the sealing element composite can be at least 55 percent, at least 60 percent, at least 65 percent, at least 70 percent, or at least 80 percent by weight based on the overall weight of the composite. Moreover, the overall amount of polylactic acid resin can be up to 98 percent, up to 90 percent, up to 85 percent, up to 80 percent, or up to 70 percent by weight based on the overall weight of the composite.

In some embodiments, the composite contains amorphous polylactic acid resin in an amount of at least 5 percent, at least 10 percent, at least 30 percent, at least 50 percent, or at least 70 percent by weight based on the overall weight of the composite. The amorphous polylactic acid resin can be present in an amount of up to 98 percent, up to 85 percent, up to 65 percent, up to 50 percent, or up to 35 percent by weight based on the overall weight of the composite.

In some embodiments, the composite contains semi-crystalline polylactic acid resin in an amount of at least 5 percent, at least 10 percent, at least 30 percent, at least 50 percent, or at least 70 percent by weight based on the overall weight of the composite.

The semi-crystalline polylactic acid resin can be present in an amount of up to 98 percent, up to 85 percent, up to 65 percent, up to 50 percent, or up to 35 percent by weight based on the overall weight of the composite.

It was discovered that certain degradants provided synergistic effects for downhole sealing applications when mixed with polylactic acid. One useful degradant is cellulose acetate propionate, a mixed cellulose ester whose degradability is related to its degree of substitution—i.e., the average number of substituent groups attached per monomeric unit. Cellulose acetate propionate can undergo hydrolysis at elevated temperatures and/or acid conditions, making it a suitable degradant in certain well stimulation operations.

In some embodiments, the cellulose acetate propionate is present in an amount of at least 2 percent, at least 10 percent, at least 25 percent, at least 35 percent, or at least 50 percent by weight based on the overall weight of the composite. In some embodiments, the cellulose acetate propionate is present in an amount of up to 95 percent, up to 75 percent, up to 55 percent, up to 40 percent, or up to 30 percent by weight based on the overall weight of the composite.

In some embodiments, the composite further comprises a swellant that enables the sealing element to increase in volume substantially when placed in contact with water or an aqueous solution. Particularly useful swellants assist in the degradation and/or dissolution of the sealing element under suitable environmental conditions. Such swellants include, for example, polyvinylpyrrolidone, starch, and combinations thereof.

In some embodiments, the swellant can provide a degree of swelling of at least 1 percent, at least 25 percent, at least 50 percent, at least 75 percent, or at least 100 percent by volume based on the original volume of the sealing element. In the same or alternative embodiments, the swellant can provide a degree of swelling of up to 209 percent, up to 175 percent, up to 150 percent, up to 125 percent, or up to 99 percent by volume based on the original volume of the sealing element.

Starches that could be incorporated into the composite of the sealing element need not be particularly restricted and may include native starches, reclaimed starches, waxy starches, modified starches, pre-gelatinized starches, or combinations thereof. In preferred embodiments, the starch is a modified starch that provides enhanced resistance to the high temperatures and pressures found deep within subterranean formations. Advantageously, the addition of a starch, such as a modified starch, was found to significantly slow degradation of composites based on polylactic acid.

Modified starches were also found to provide enhanced compatibility amongst the components in the composite material. Evidence for this is given by the melt flow measurements of composites containing modified starch as reported in the Examples. Generally, the greater the compatibility of the starch within the formulation, the greater its plasticization effect, resulting in a higher MFI. Compatibility is an important factor in providing a high degree of integrity and impact resistance in the

final, compounded sealing element. Furthermore, a high MFI can enhance the ability to process these composite materials in the melt, such as by extrusion and injection molding.

Useful modified starches can include acid-treated starch, alkaline-treated starch, bleached starch, oxidized starch, enzyme-treated starch, monostarch phosphate, distarch phosphate, phosphated distarch phosphate, acetylated distarch phosphate, starch acetate, acetylated distarch adipate, dextrin, cyclodextrin, hydroxypropyl starch, hydroxypropyl distarch phosphate, hydroxypropyl distarch glycerol, starch sodium octenyl succinate, acetylated oxidized starch, and combinations thereof.

In some embodiments, the starch is present in an amount of at least 0.5 percent, at least 5 percent, at least 15 percent, at least 20 percent, or at least 30 percent by weight based on the overall weight of the composite. In some embodiments, the starch is present in an amount of up to 20 percent, up to 30 percent, up to 35 percent, up to 40 percent, or up to 50 percent by weight based on the overall weight of the composite.

It can be advantageous for the composite to further include a degradant that assists in chemically-induced degradation of the composite. It can be beneficial if such degradation occurs exclusively under some environments but not others. It is further beneficial if these environments can be changed relatively quickly and easily, enabling the operator to unblock perforations or passageways occluded by the sealing element "on demand."

Examples of suitable degradants may include, but are not limited to, carboxylic acids such as formic acid, acetic acid, oxalic acid, glyoxylic acid, glycolic acid, propionic acid, acrylic acid, malonic acid, pyruvic acid, lactic acid, butyric acid, isobutyric acid, succinic acid, acetoacetic acid, fumaric acid, maleic acid, oxaloacetic acid, malic acid, tartaric acid, crotonic acid, valeric acid, glutaric acid, α -ketoglutaric acid, caproic acid, adipic acid, citric acid, aconitic acid, isocitric acid, sorbic acid, enanthic acid, pimelic acid, benzoic acid, salicylic acid, pelargonic acid, trimesic acid, cinnamic acid, capric acid, sebacic acid. Combinations of the above are also possible.

Alternatively, or in combination, the degradant (e.g., citric acid) can be present in the fracturing fluid injected downhole to initiate or accelerate degradation of the sealing element.

Inclusion of the degradant in the composite is generally preferred over mixing the degradant into a fracturing fluid for several reasons. First, the former is more efficient than the latter from a mass transfer perspective because it disposes the degradant adjacent to the polylactic acid matrix where it can immediately actuate the degradation reaction. Second, the degradant can be intimately dispersed throughout the composite material, enabling the degradation reaction to occur in the bulk of the composite as well as on the surface. When used in combination with a suitable swellant, water uptake by the composite can enable facile degradation of the sealing element from the inside out. Third, it is not necessary for the degradant to contact other portions of the wellbore, reducing the overall amount of degradant needed and mitigating any environmental impact that may be caused by the degradant.

The degradant can be present in an amount of at least 0.1 percent, at least 1 percent, at least 5 percent, at least 7 percent, or at least 10 percent by weight based on the overall weight of the composite.

On the upper end, the degradant can be present in an amount of up to 20 percent, up to 16 percent, up to 12 percent, up to 10 percent, or up to 8 percent by weight based on the overall weight of the composite.

Where present in the fracturing fluid, the degradant can be present in an amount of at least 0.1 percent, at least 1 percent, at least 5 percent, at least 7 percent, or at least 10 percent based on the overall weight of the fracturing fluid. Further, the degradant can be present in an amount of up to 20 percent, up to 16 percent, up to 12 percent, up to 10 percent, or up to 8 percent by weight based on the overall weight of the fracturing fluid.

Yet another optional component in the composite is a plasticizer, which can impart improved resilience and strength in the sealing element. A plasticizer can also enhance compatibility of the melt blend components, improve processing characteristics in the blending and processing steps, and regulate the rate at which the sealing element degrades. One preferred plasticizer is acetyl tributyl citrate, which has a low toxicity and volatility and is also compatible with many bio-plastics such as a polylactic acid, cellulose acetate propionate, polyhydroxyalkanoic and other acid resins.

The plasticizer can be present in an amount of at least 0.1 percent, at least 1 percent, at least 10 percent, at least 15 percent, or at least 20 percent by weight based on the overall weight of the composite. The plasticizer can be present in an amount of up to 12 percent, up to 17 percent, up to 22 percent, up to 26 percent, or up to 30 percent by weight based on the overall weight of the composite.

Optionally but not shown, the sealing element may have a layered structure comprised of two or more composite materials, where the layered structure includes one or more chemically distinct layers. The one or more layers could be disposed on a core having a composition that is different from at least one of the layers disposed thereon. Each layer may fully surround the underlying core or layer or alternatively may only extend over merely a portion of the underlying core or layer.

Suitable layers may include, but are not limited to, variants of the composite compositions disclosed herein, additional filler materials and additives, and mixtures thereof.

It is understood that the sealing elements described herein may further include any of a number of other degradable polymeric resins, filler materials, degradants, or plasticizers.

Exemplary degradable polymeric resins include, but are not limited to, polyglycolic acid, cellulose acetate, and cellulose acetate butyrate.

Useful filler materials can include reinforcement agents that increase the mechanical strength and/or toughness of the composite. Exemplary suitable reinforcing agents include, but are not limited to, talc, mica, pulp, calcium carbonate, fiberglass, glass, phenolic, quartz (and other inorganic material) spheres, carbon fibers, carbon black, ceramic fibers, nylon fibers, polyethylene terephthalate ("PET") fibers, and silica.

The aforementioned sealing elements can be made using any known process, such as injection molding, casting, extrusion, milling, grinding, and layer-by-layer additive manufacturing. Further, the sealing elements can have any known three-dimensional shape suitable for use in subterranean well operations. Aspects of manufacturing and processing degradable composite materials are described, for example, in U.S. Patent Publication No. 2013/0292123 (Murphree et al.).

While not intended to be exhaustive, particular embodiments of the provided sealing elements and methods associated thereof are enumerated below.

1. A sealing element for sealing at least a portion of a well for a hydraulic fracturing process, the sealing element made from a composite comprising: an amorphous polylactic acid resin; and cellulose acetate propionate.
2. The sealing element of embodiment 1, wherein the cellulose acetate propionate is present in an amount of from 2 percent to 95 percent by weight, based on the overall weight of the composite.
3. The sealing element of embodiment 2, wherein the cellulose acetate propionate is present in an amount of from 50 percent to 95 percent by weight, based on the overall weight of the composite.
4. The sealing element of embodiment 2, wherein the cellulose acetate propionate is present in an amount of from 25 percent to 55 percent by weight, based on the overall weight of the composite.
5. The sealing element of embodiment 2, wherein the cellulose acetate propionate is present in an amount of from 2 percent to 30 percent by weight, based on the overall weight of the composite.
6. The sealing element of any one of embodiments 1-5, wherein the amorphous polylactic acid resin is present in an amount of from 5 percent to 98 percent by weight, based on the overall weight of the composite.
7. The sealing element of embodiment 6, wherein the amorphous polylactic acid resin is present in an amount of from 70 percent to 98 percent by weight, based on the overall weight of the composite.
8. The sealing element of embodiment 6, wherein the amorphous polylactic acid resin is present in an amount of from 30 percent to 75 percent by weight, based on the overall weight of the composite.
9. The sealing element of embodiment 6, wherein the amorphous polylactic acid resin is present in an amount of from 5 percent to 35 percent by weight, based on the overall weight of the composite.
10. The sealing element of any one of embodiments 1-9, wherein the sealing element further comprises a semi-crystalline polylactic acid resin.
11. The sealing element of embodiment 10, wherein the semi-crystalline polylactic acid resin is present in an amount of from 5 percent to 98 percent by weight, based on the overall weight of the composite.
12. The sealing element of embodiment 11, wherein the semi-crystalline polylactic acid resin is present in an amount of from 70 percent to 98 percent by weight, based on the overall weight of the composite.
13. The sealing element of embodiment 11, wherein the semi-crystalline polylactic acid resin is present in an amount of from 30 percent to 75 percent by weight, based on the overall weight of the composite.
14. The sealing element of embodiment 11, wherein the semi-crystalline polylactic acid resin is present in an amount of from 5 percent to 35 percent by weight, based on the overall weight of the composite.
15. The sealing element of any one of embodiments 1-14, wherein the composite further comprises a swellant selected from starch, polyvinylpyrrolidone, and combinations thereof.

16. The sealing element of embodiment 15, wherein the starch comprises a native starch, reembodimented starch, waxy starch, modified starch, pre-gelatinized starch, or combination thereof.
17. The sealing element of embodiment 16, wherein the starch is a modified starch comprising dextrin, cyclodextrin, acid-treated starch, alkaline-treated starch, bleached starch, oxidized starch, enzyme-treated starch, monostarch phosphate, distarch phosphate, phosphated distarch phosphate, acetylated distarch phosphate, starch acetate, acetylated distarch adipate, hydroxypropyl starch, hydroxypropyl distarch phosphate, hydroxypropyl distarch glycerol, starch sodium octenyl succinate, acetylated oxidized starch, or a combination thereof.
18. The sealing element of any one of embodiments 15-17, wherein the swellant is present in an amount of from 0.5 percent to 20 percent by weight, based on the overall weight of the composite.
19. The sealing element of embodiment 15-17, wherein the swellant is present in an amount of from 15 percent to 35 percent by weight, based on the overall weight of the composite.
20. The sealing element of embodiment 15-17, wherein the swellant is present in an amount of from 30 percent to 50 percent by weight, based on the overall weight of the sealing element.
21. The sealing element of any one of embodiments 1-20, wherein the composite is generally solid.
22. A sealing element for sealing at least a portion of a well for a hydraulic fracturing process, the sealing element made from a composite comprising: a polylactic acid resin; a swellant comprising polyvinylpyrrolidone; and optionally, citric acid.
23. A sealing element for sealing at least a portion of a well for a hydraulic fracturing process, the sealing element made from a composite comprising: a polylactic acid resin; a swellant selected from modified starch, polyvinylpyrrolidone, and combinations thereof; and citric acid.
24. A sealing element for sealing at least a portion of a well for a hydraulic fracturing process, the sealing element made from a composite comprising: a polylactic acid resin; and a swellant comprising modified starch, wherein the composite is generally solid.
25. The sealing element of embodiment 24, wherein the composite further comprises a carboxylic acid.
26. The sealing element of embodiment 25, wherein the carboxylic acid is citric acid.
27. The sealing element of embodiment 22, 23 or 26, wherein the citric acid is present in an amount of from 0.1 percent to 8 percent by weight, based on the overall weight of the composite.
28. The sealing element of embodiment 22, 23 or 26, wherein the citric acid is present in an amount of from 5 percent to 12 percent by weight, based on the overall weight of the composite.
29. The sealing element of embodiment 22, 23 or 26, wherein the citric acid is present in an amount of from 10 percent to 20 percent by weight, based on the overall weight of the composite.
30. The sealing element of any one of embodiments 22-29, wherein the polylactic acid resin is present in an amount of from 80 percent to 98 percent by weight, based on the overall weight of the composite.

31. The sealing element of any one of embodiments 22-29, wherein the polylactic acid resin is present in an amount of from 65 percent to 85 percent by weight, based on the overall weight of the composite.
32. The sealing element of any one of embodiments 22-29, wherein the polylactic acid resin is present in an amount of from 55 percent to 70 percent by weight, based on the overall weight of the composite.
33. The sealing element of any one of embodiments 22-32, wherein the swellant is present in an amount of from 0.5 percent to 20 percent by weight, based on the overall weight of the composite.
34. The sealing element of any one of embodiments 22-32, wherein the swellant is present in an amount of from 15 percent to 35 percent by weight, based on the overall weight of the composite.
35. The sealing element of any one of embodiments 22-32, wherein the swellant is present in an amount of from 30 percent to 50 percent by weight, based on the overall weight of the sealing element.
36. The sealing element of any one of embodiments 22-35, wherein the modified starch comprises dextrin, cyclodextrin, acid-treated starch, alkaline-treated starch, bleached starch, oxidized starch, enzyme-treated starch, monostarch phosphate, distarch phosphate, phosphated distarch phosphate, acetylated distarch phosphate, starch acetate, acetylated distarch adipate, hydroxypropyl starch, hydroxypropyl distarch phosphate, hydroxypropyl distarch glycerol, starch sodium octenyl succinate, acetylated oxidized starch, or a combination thereof.
37. The sealing element of any one of embodiments 22-36, wherein the composite is generally solid.
38. The sealing element of any one of embodiments 1-37, wherein the composite is macroscopically homogenous.
39. The sealing element of any one of embodiments 1-38, wherein the sealing element further comprises a plasticizer.
40. The sealing element of embodiment 39, wherein the plasticizer comprises acetyl tributyl citrate.
41. The sealing element of embodiment 39 or 40, wherein the plasticizer is present in an amount of from 0.1 percent to 12 percent by weight, based on the overall weight of the composite.
42. The sealing element of embodiment 39 or 40, wherein the plasticizer is present in an amount of from 10 percent to 22 percent by weight, based on the overall weight of the composite.
43. The sealing element of embodiment 39 or 40, wherein the plasticizer is present in an amount of from 20 percent to 30 percent by weight, based on the overall weight of the composite.
44. The sealing element of any one of embodiments 1-43, wherein the composite is a monolithic composite having a spherical shape defining the shape of the sealing element.
45. The sealing element of any one of embodiments 1-43, wherein the composite is granular.
46. The sealing element of embodiment 45, wherein the composite is comprised of particles having generally flake-like shapes.
47. The sealing element of any one of embodiments 1-46, wherein the sealing element is injection molded, machined, milled, strand pelletized, underwater pelletized, or ground.

48. A method of sealing at least a portion of a well for a hydraulic fracturing process comprising: placing the sealing element of any one of embodiments 1-47 against a perforation or constriction within the well, the perforation or constriction having a smaller cross-section than the sealing element to restrict fluid communication between a first segment and a second segment of the well; and degrading the sealing element to restore the fluid communication between the first and second segments.

49. The method of embodiment 48, wherein degrading the sealing element comprises exposing the sealing element to a fracturing fluid at a temperature of from 50°C to 95°C and a pressure of 0.1 to 80 MPa.

50. The method of embodiment 48, wherein degrading the sealing element comprises exposing the sealing element to the fracturing fluid at a temperature of from 90°C to 135°C and a pressure of 0.1 to 80 MPa.

51. The method of embodiment 48, wherein degrading the sealing element comprises exposing the sealing element to the fracturing fluid at a temperature of from 130°C to 170°C and a pressure of 0.1 to 80 MPa.

52. The method of any one of embodiments 49-51, wherein the fracturing fluid comprises water.

53. The method of any one of embodiments 49-52, wherein the fracturing fluid comprises citric acid.

54. The method of embodiment 53, wherein the citric acid is present in an amount of from 0.1 percent to 8 percent by weight relative to the overall weight of the fracturing fluid.

55. The method of embodiment 53, wherein the citric acid is present in an amount of from 5 percent to 12 percent by weight relative to the overall weight of the fracturing fluid.

56. The method of embodiment 53, wherein the citric acid is present in an amount of from 10 percent to 20 percent by weight relative to the overall weight of the fracturing fluid.

EXAMPLES

Objects and advantages of this disclosure are further illustrated by the following non-limiting examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this disclosure. Unless otherwise noted, all parts, percentages, ratios, etc. in the Examples and the rest of the specification are by weight.

Materials

“PLA 6252,” a polylactic acid resin, was obtained from NatureWorks, Minnetonka, MN, under the trade designation “Inego™ Biopolymer 6252D.”

“PLA 6361,” a polylactic acid resin, was obtained from NatureWorks, Minnetonka, MN, under the trade designation “Inego™ Biopolymer 6361D.”

“PLA 4032,” a polylactic acid resin, was obtained from NatureWorks, Minnetonka, MN, under the trade designation “Inego™ Biopolymer 4032D.”

“PLA 4060,” a polylactic acid resin, was obtained from NatureWorks, Minnetonka, MN, under the trade designation “Inego™ Biopolymer 4060D.”

“CAP” was obtained from Eastman™, Kingsport, TN, under the trade designation “Cellulose Acetate Propionate 482-20.”

“Glycan Starch,” a modified starch, was obtained from Glycan BioTechnology Co., Taoyuan, Taiwan under the trade designation “SR-088.”

5 “Corn Starch,” a corn starch powder, was obtained from Fischer Scientific, Fair Lawn, NJ, under the trade designation “Corn Starch Powder S-510.”

“Potato Starch,” a potato starch powder, was obtained from Spectrum Chemical, Gardena, CA, under the trade designation “Potato Starch Powder S1553.”

10 “Citric Acid,” a granulated citric acid, was obtained from Brenntag Great Lakes, Wauwatosa, WI under the trade designation “Citric Acid Monohydrate USP.”

“PVP,” a polyvinylpyrrolidone resin, was obtained from Ashland Specialty Ingredients, Wilmington, DE, under the trade designation “Disintex™ 200.”

“Ultra Talc 609,” an ultrafine ground talc, was obtained from Barretts Minerals, Inc., Bethlehem, PA, under the trade designation “Ultratac® 609.”

15 The following abbreviations are used: g = gram, h = hour, min=minute, m = meter, cm = centimeter, mm = millimeter, ml = milliliter, V = volt, mV = millivolt, kN = kilonewton, Hz = hertz, MPa = megapascals, GPa = gigapascals, J=joule, kJ = kilojoule, wt=weight, and NM = not measured.

Methods for Preparing Samples

20 Samples for Examples 1, 8 and 9 through 17 were prepared for testing by compounding the desired ingredients in the ratios described in Tables 1 and 2 below using an 18mm Berstoff Twin screw extruder (KraussMaffei Technologies GmbH, Munich, Germany), followed by underwater pelletizing to form pellets of approximately 3 mm diameter. Ingredients were heated to a temperature of 180°C during compounding.

25 Samples for Comparatives A, B, C and D and Examples 2 through 7 were prepared for testing by heating and mixing ingredients in a Brabender compounder (C.W. Brabender Instruments, Inc.). Ingredients were added in the relative amounts described in Table 1 to provide sample sizes of approximately 60 g. Ingredients were heated to a temperature of 180°C during compounding.

Table 1

Comparative				
	A	B	C	D
Component	wt %	wt %	wt %	wt %
PLA 6252 – semi-crystalline	59	60	59	60
PLA 6361 – amorphous	20	20	20	20
CAP 482-20 –				

cellulose acetate propionate				
Glycan Starch (SR-088)				
Potato Starch	20	20		
Corn Starch			20	20
Citric Acid granules	1		1	
PVP – Poly- vinylpyrrolidone				

Table 1-Continued

Example								
	1	2	3	4	5	6	7	8
Component	wt %	wt %	wt %	wt %	wt %	wt %	wt %	wt %
PLA 6252 – semi-crystalline	60	59	60	65	60	55	50	
PLA 6361 – amorphous	20	20	20	30	25	20	15	15
CAP 482-20 – cellulose acetate propionate								75
Glycan Starch (SR-088)	20	20	20			20	20	10
Potato Starch								
Corn Starch								
Citric Acid granules		1						
PVP – Poly- vinylpyrrolidone				5	15	5	15	

Table 2

Example										
	9	10	11	12	13	14	15	16	17	18
Component	wt %	wt %	wt %	wt %	wt %	wt %	wt %	wt %	wt %	wt %
PLA 6252 – semi-crystalline	44	55	45							
PLA 6361 – amorphous	15	20	15	10	10					
PLA 4032 – semi-crystalline						80	75	80	17	75
CAP 482-20 – cellulose acetate propionate				75	60	17	22	15	80	21
Glycan Starch (SR-088)	20	20	20	10	10	3	3	5	3	3
Ultra Talc 609	20	5	20	5	20					1
Citric Acid granules	1									

Table 2 - Continued

Example			
	19	20	21
Component	wt %	wt %	wt %
PLA 4032 – semi-crystalline	48	36	14
PLA 4060 – amorphous	16	12	
CAP 482-20 – cellulose acetate propionate	12	9	64
Glycan Starch (SR-088)	4	3	2
Ultra Talc 609	20	40	20

Method for Measuring Mass Change and Volume Change

For each mass change measurement, approximately 1 g of the desired sample was placed in a 20 ml headspace vial from Agilent Company (5301 Stevens Creek Blvd. Santa Clara, CA, 95051 United States). The vial was filled with deionized water, capped, and placed in a Parr Oxygen Bomb calorimeter from Parr Instruments (211 Fifty Third Street, Moline, Illinois 61265-1770). The calorimeter was then filled with distilled water, sealed and placed in a Despatch Oven, Protocol 3, from Despatch Industries (8860 207th Street West, Minneapolis, MN 55044), at a desired temperature. Experimental times reported in the tables below indicate the time elapsed after samples were placed in the oven.

At the end of the desired experimental time, the calorimeter was removed from the oven and placed under running water for a period of approximately 15 min to cool. The calorimeter was then carefully opened and the vials were removed. Visual observations were made and recorded. The vials were then individually opened and the solution discarded. The remaining sample was patted dry with paper towel. The final sample mass was then measured.

For Examples 1 and 8, volume change was determined by the following procedure. Prior to placement in a headspace vial, 3 to 5 diameter measurements were made with calipers at different circumferences around each of five pellets of the same Example material. The diameters were used to calculate volumes by the formula: $\text{volume} = 4/3 \pi (\text{diameter} / 2)^3$. The calculated volumes for each pellet were averaged and the five average pellet volumes for the five pellets for each Example material measured were averaged. This determination of average pellet volume was repeated after dissolvability testing. For both Example 1 and Example 8, the average initial volume was subtracted from the average final volume and the result of this subtraction was divided by the average initial volume. The result of this division was multiplied by 100.

Mass change, reported in the table below as “% Mass Change,” was calculated by subtracting the initial sample mass after drying from the final sample mass, dividing the difference by the initial sample mass, and multiplying the result of this division by 100.

Methods for Measuring Mechanical Properties

Specimens for mechanical property measurements were made by injection molding pellets using a BOY 22D. Measurements were made using a MTS Universal Testing System, Criterion Model 43.

Compressibility of injection molded cylindrical specimens with a diameter of 6.4 mm for Examples 1 and 8 through 13 was measured according to ASTM method D610813 at ambient temperature and 80°C with the following deviations:

- a 50 kN load cell was used (model number LPS.504, having a sensitivity of 2.120 mV/V)
- test speed was 1 mm/min

The stopping condition was defined as when primary strain exceeded the strain endpoint of 50%. Compressibility measurements at 80°C were carried out inside a Thermacraft LBO-Series Box laboratory oven.

Flexural modulus, flexural strength, tensile strength, tensile elongation, and tensile modulus were measured for Examples 1 and 8 through 17 using a 5kN load cell, model number LPS.503, having a sensitivity of 2.380 mV/V. Flexural modulus and flexural strength were measured using a three-point bend test method ASTM D790-10 with the following deviations:

- 5 • test speed was 5.08 mm/min
- data acquisition rate was 10 Hz

The stopping condition was defined as when the primary strain exceeded the strain endpoint of 8%.

10 Tensile strength, tensile elongation, and tensile modulus were measured for Examples 1 and 8 through 17 using ASTM D638-14, for samples having dimensions of 1.27 cm width, 0.3175 cm thickness and 16.51 cm length, with a narrow section of length 6.35 cm, with the following deviations:

- test speed was 50.8 mm/min
- data acquisition rate was 10 Hz

15 Impact strength was measured for Examples 1 and 8 through 17 using a model IT 503 Plastic Impact tester (Tinius Olsen). Measurements were made using both ASTM D256, Notched Izod Impact Test Method, and ASTM D6110, Notched Charpy Impact Test Method. Specimens were notched with a model 899 notcher (Tinius Olsen).

Methods for Measuring Melt Flow

20 Melt Flow Index (MFI) of Comparatives B and D and Example 3 was determined using ASTM D1238-10 Procedure A and performed on an Extrusion Plastometer, model MP600, from Tinius-Olsen (Horsham, PA).

Characterization of Comparatives A, B, C, and D and Examples 1 through 8

25 Sample materials were prepared by the methods described above, with the compositions described in Table 1. They were tested for mass change and volume change according to the above methods. Mass change and volume change measurement results are provided in Tables 3 through 8 below. After 168 h of experimental time at 100°C, Comparatives A, B, C and D had completely dissolved.

30 Mass change results for Examples 2 and 3 and Comparatives A, B, C, and D exposed to an experimental temperature of 100°C are provided in Table 3 below. Examples 2 and 3 comprised glycan starch. Comparatives A and B comprised potato starch. Comparatives C and D comprised corn starch. The mass increase for Example 2, which comprised citric acid, was smaller than the mass increase at the same experimental time for Example 3, which did not comprise citric acid, at both 3 h and 6 h of
35 experimental treatment. This relationship was observed for Comparatives A and B, both comprising potato starch and Comparative A comprising citric acid, and for Comparatives C and D, both comprising corn starch, and Comparative C comprising citric acid.

Table 3

Example or Comparative	3 h	6 h	16 h	24 h	72h	168 h
	% Mass Change, 100°C					
2	3	3	-5	-8	-14	-89
3	8	6	-4	-9	-13	-81
A	5	2	-7	-13	-18	-100
B	8	8	-4	-13	-20	-100
C	5	1	-10	-15	-17	-100
D	8	9	-3	-8	-14	-100

The mass changes observed with increasing experimental time for Examples 1 and 8 are provided in Tables 4, 5 and 6 below. For illustrative purposes, a plot of the data in Table 4 is provided in FIG. 3.

- 5 For Example 1, comprising semi-crystalline PLA, amorphous PLA and starch, a greater mass increase is observed for experimental times of 1 h to 6 h at the experimental temperature of 80°C than at the experimental temperature of 60°C. At experimental times of 72 h and 168 h, a decrease in mass is observed for Example 1 with exposure to the experimental temperature of 80°C. For Example 8,
- 10 comprising amorphous PLA, CAP, and starch, an increase of mass was observed with 168 h of experimental time at the experimental temperature of 120°C. At the experimental temperature of 150°C, a mass increase was observed after 2.5 h of experimental time and a mass loss was observed after 72 h of experimental time for Example 8.

Table 4

Example 1	% Mass Change, 80°C	% Mass Change, 60°C
Time (h)		
0.5	1	2
1	5	3
1.5	6	4
2	6	3
2.5	8	5
3	8	5
3.5	8	6
4	8	6
4.5	9	7
5	9	7
5.5	10	6
6	9	7
8	8	9
16	7	9
24	5	9
72	-4	6
168	-10	8

Table 5

Example 8	% Mass Change, 120°C
Time (h)	
0.5	5
1	11
1.5	15
2	18
2.5	16
3	19
3.5	22
4	23
4.5	26
5	29
5.5	31
13	60
16	81
24	128
72	209
168	329

Table 6

Example 8	% Mass Change, 150°C
Time (h)	
0.5	7
1	15
1.5	20
2	24
2.5	26
3	24
4	19
4.5	20
5	13
5.5	10
8	17
16	10
24	-60
48	-86
72	-85

As provided in Table 7 below, exposure of Example 1 to an experimental temperature of 80°C for an experimental time of 3 h resulted in a mass increase of 22% and a volume increase of 23%. Exposure of Example 8 to an experimental temperature of 150°C for an experimental time of 3 h resulted in a mass increase of 8% and a volume increase of 7%. The correlation of increased volume for these samples with increased measured mass indicates that, for the present Examples, mass change may be understood to correlate linearly with volume change.

Table 7

Example	Temperature	Time	% Mass Change	% Volume Change
1	80°C	3h	22	23
8	150°C	3h	8	7

The mass change measurements for Examples 4, 5, 6, and 7, measured for increasing experimental times at the experimental temperature of 100°C are provided in Table 8 below. The mass increases observed for Examples 6 and 7 over 3 h experimental time at an experimental temperature of 100°C were greater than those observed for the same experimental times at the same experimental temperature for Examples 4 and 5.

Table 8

Example	0.5 h	1 h	1.5 h	2 h	2.5 h	3 h
	% Mass Change, 100°C					
4	5	3	4	4	4	4
5	6	9	8	7	5	4
6	17	20	38	52	32	35
7	66	61	60	58	23	61

The theoretical pressure inside the calorimeter at each experimental temperature used in the mass change measurements is provided in Table 9 below.

Table 9

Temperature (°C)	Theoretical Pressure (MPa)
60	0.02
80	0.05
100	0.1
120	0.2
150	0.5

MFI measurements are provided in Table 10 below:

Table 10

Example or Comparative	MFI (g/10 min)
3	110.05
B	82.29
D	84.46

Characterization of Examples 1 and 8 through 17

Sample materials were prepared by the methods described above, with the compositions described in Tables 1 and 2. Sample materials were tested for mechanical properties according to the above methods. Compression measurement results are provided in Table 11 below. Tensile, flexural, and impact measurement results are provided in Table 12 below.

Table 11

Example	Compression Modulus 25°C (GPa)	Yield Stress 25°C (MPa)	Compression Modulus 80°C (GPa)	Yield Stress 80°C (MPa)
1	2.0	69.6	0.2	6.7
8	1.4	49.6	0.6	17.7
9	1.8	53.4	0.1	4.3
10	2.0	68.9	0.2	6.7
11	2.0	63.2	0.2	7.3
12	1.4	49.0	0.6	17.7
13	1.8	52.3	0.8	18.8
14	2.15	81.17	0.22	13.01
15	2.13	79.90	0.36	24.46
16	2.25	83.99	0.22	15.15
17	1.64	57.89	0.72	21.95
18	2.17	80.66	0.02	3.863
19	2.71	85.27	0.009	2.159
20	3.55	82.45	0.030	4.138
21	2.16	65.44	1.021	24.50

Table 12

Example	Tensile Strength (MPa)	Tensile Elongation (%)	Tensile Modulus (GPa)	Flexural Modulus (GPa)	Flexural Strength (MPa)	Charpy Impact Strength (kJ/m ²)	Izod Impact Strength (J/m)
1	39.2	4.2	1.3	4.2	46.3	2.9	21.5
8	53.0	16.4	1.1	2.5	72.9	3.6	29.9
9	37.7	4.0	1.4	3.2	56.9	1.9	12.0
10	41.8	5.0	1.2	2.9	65.3	2.9	25.6
11	33.9	3.3	1.5	3.2	58.6	1.9	12.2
12	51.6	21.3	1.0	2.1	71.7	4.8	35.4
13	51.5	6.6	1.5	3.4	73.5	3.4	24.8
14	70.2	7.7	1.3	2.9	97.3	2.7	35.2
15	69.5	7.7	1.2	3.0	99.3	2.5	27.0
16	70.7	7.6	1.2	3.5	104.4	2.6	29.2
17	61.0	16.7	0.99	2.4	87.6	5.6	34.2
19	57.1	5.225	1.730	4.563	89.1	2.62	24.8
20	58.6	3.780	2.595	7.555	89.1	2.08	12.4
21	63.8	8.512	1.477	3.627	93.8	3.00	31.5

CLAIMS:

What is claimed is:

1. A sealing element for sealing at least a portion of a well for a hydraulic fracturing process, the sealing element made from a composite comprising:
an amorphous polylactic acid resin; and cellulose acetate propionate.
2. The sealing element of claim 1, wherein the cellulose acetate propionate is present in an amount of from 2 percent to 95 percent by weight, based on the overall weight of the composite.
3. The sealing element of claim 1 or 2, wherein the sealing element further comprises a semi-crystalline polylactic acid resin.
4. The sealing element of any one of claims 1-3, wherein the composite further comprises a swellant selected from starch, polyvinylpyrrolidone, and combinations thereof.
5. A sealing element for sealing at least a portion of a well for a hydraulic fracturing process, the sealing element made from a composite comprising:
a polylactic acid resin;
a swellant selected from modified starch, polyvinylpyrrolidone, and combinations thereof; and citric acid.
6. The sealing element of claim 4 or 5, wherein the swellant is a modified starch comprising dextrin, cyclodextrin, acid-treated starch, alkaline-treated starch, bleached starch, oxidized starch, enzyme-treated starch, monostarch phosphate, distarch phosphate, phosphated distarch phosphate, acetylated distarch phosphate, starch acetate, acetylated distarch adipate, hydroxypropyl starch, hydroxypropyl distarch phosphate, hydroxypropyl distarch glycerol, starch sodium octenyl succinate, acetylated oxidized starch, or a combination thereof.
7. The sealing element of any one of claims 4-6, wherein the swellant is present in an amount of from 0.5 percent to 50 percent by weight, based on the overall weight of the composite.
8. A sealing element for sealing at least a portion of a well for a hydraulic fracturing process, the sealing element made from a composite comprising:
a polylactic acid resin; and a swellant comprising modified starch, wherein the composite is generally solid.

9. The sealing element of claim 8, wherein the composite further comprises a carboxylic acid.
10. The sealing element of claim 9, wherein the carboxylic acid is citric acid.
11. The sealing element of any one of claims 1-10, wherein the sealing element further comprises a plasticizer, the plasticizer comprising acetyl tributyl citrate.
12. A method of sealing at least a portion of a well for a hydraulic fracturing process comprising:
placing the sealing element of any one of claims 1-11 against a perforation or passageway within the well, the perforation or passageway having a smaller cross-section than the sealing element to restrict fluid communication between a first segment and a second segment of the well; and
degrading the sealing element to restore the fluid communication between the first and second segments.
13. The method of claim 12, wherein degrading the sealing element comprises exposing the sealing element to a fracturing fluid at a temperature of from 50°C to 170°C and a pressure of 0.1 to 80 MPa.
14. The method of claim 13, wherein the fracturing fluid comprises citric acid.
15. A sealing element for sealing at least a portion of a well for a hydraulic fracturing process, the sealing element made from a composite comprising:
a polylactic acid resin; and
a swellant comprising polyvinylpyrrolidone.

1/2

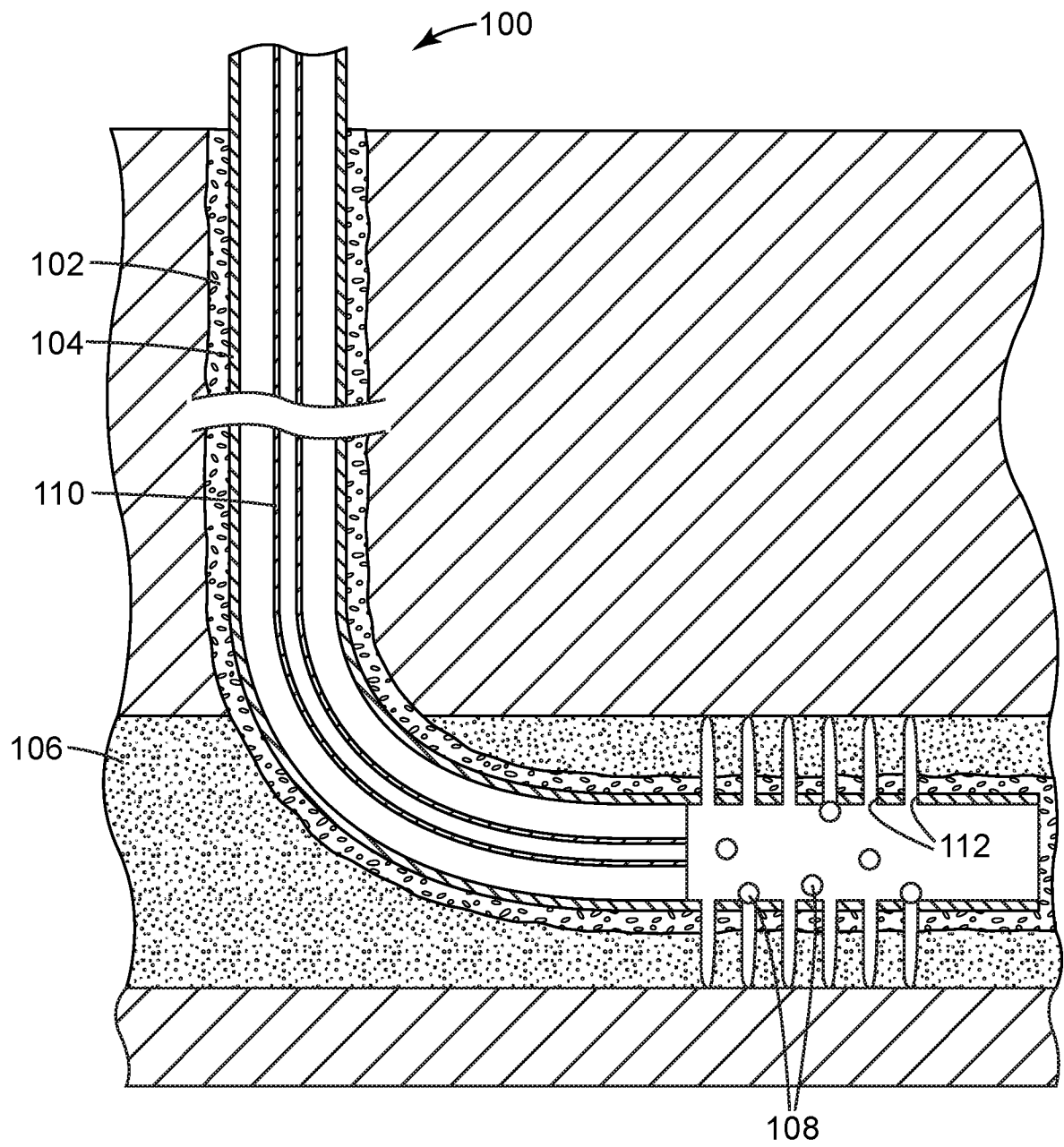
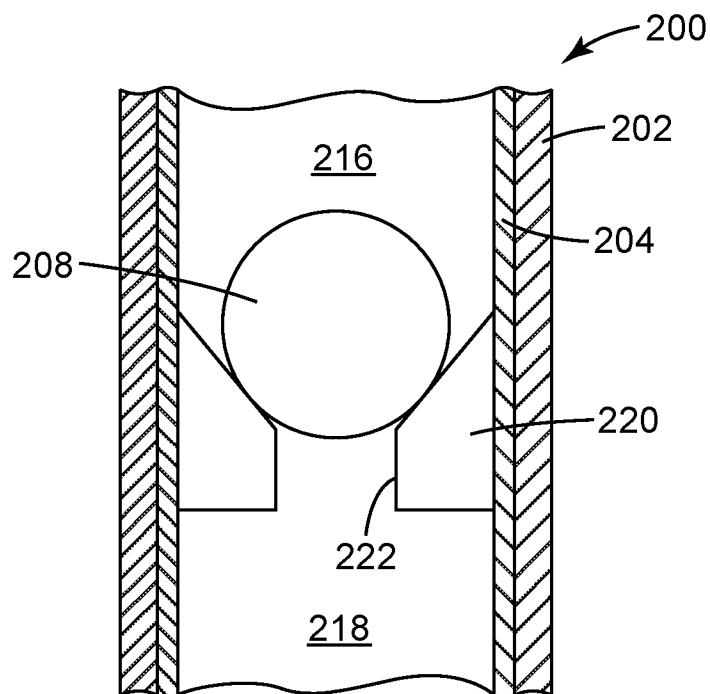
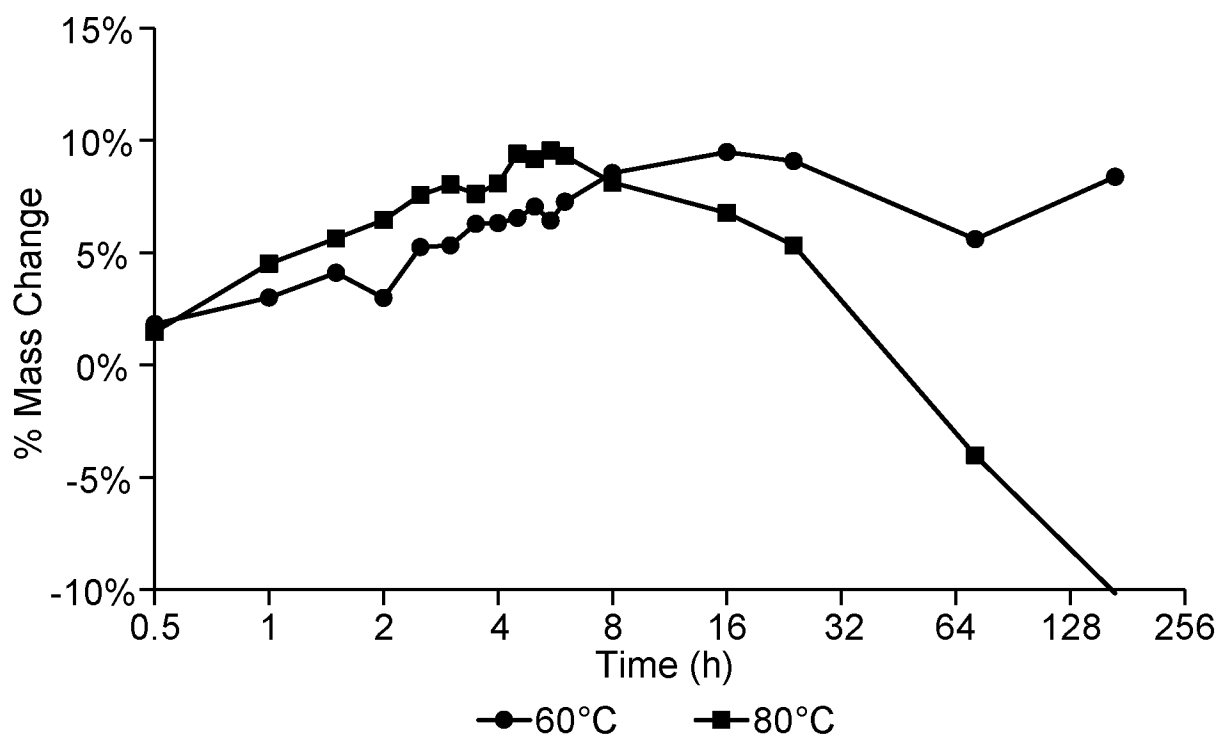


Fig. 1

2/2

*Fig. 2**Fig. 3*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/053095**A. CLASSIFICATION OF SUBJECT MATTER****E21B 34/06(2006.01)i, E21B 41/00(2006.01)i, E21B 43/26(2006.01)i, E21B 43/17(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)

E21B 34/06; E21B 33/00; C09K 8/44; E21B 19/24; C09K 8/64; E21B 43/25; E21B 43/16; C09K 8/20; E21B 41/00; E21B 43/26; E21B 43/17

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: hydraulic fracturing, seal, polylactic acid, cellulose, swellant, modified starch, degrade

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2013-0233546 A1 (LIANG et al.) 12 September 2013 See paragraphs [0001], [0012], [0027]-[0039], [0054].	1-3, 12-15
Y		4-11
Y	US 2010-0036017 A1 (EOFF et al.) 11 February 2010 See paragraphs [0072]-[0077], [0109], [0127].	4-11
A	WO 2013-048643 A1 (BAKER HUGHES INCORPORATED) 04 April 2013 See paragraphs [0030]-[0034] and figures 4A-4B.	1-15
A	US 2015-0060072 A1 (SCHLUMBERGER TECHNOLOGY CORPORATION) 05 March 2015 See paragraphs [0089], [0103]-[0119], [0167]-[0175].	1-15
A	US 2010-0323932 A1 (BUSTOS et al.) 23 December 2010 See paragraphs [0023]-[0049].	1-15



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

28 December 2016 (28.12.2016)

Date of mailing of the international search report

28 December 2016 (28.12.2016)

Name and mailing address of the ISA/KR

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

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