CLAIMS

What is claimed is:

1. A method of treating a subterranean formation, the method comprising:

obtaining or providing a composition comprising:

- a crosslinkable viscosifier polymer comprising an ethylene repeating unit comprising a $-C(O)NH_2$ group; and an ethylene repeating unit comprising an $-S(O)_2OR^1$ group, wherein:
  - at each occurrence R^1 is independently selected from the group consisting of -H and a counterion; and
  - the repeating units are in block, alternate, or random configuration; and
- at least one crosslinker;

placing the composition in a subterranean formation downhole; and

crosslinking the composition downhole,

wherein the crosslinkable viscosifier polymer has about Z^1 mol% of the ethylene repeating unit comprising the $-C(O)NH_2$ group and has about N^1 mol% of the ethylene repeating unit comprising the $-S(O)_2R^1$ group, wherein:

- Z^1 is about 10% to about 90%, and N^1 is about 10% to about 90%;
- Z^1 is about 30% to about 50%, and N^1 is about 30% to about 50%; or
- $Z^1 + N^1$ is about 100%.

2. The method of claim 1, wherein:

- the obtaining or providing of the composition occurs above-surface;
- the obtaining or providing of the composition occurs downhole;
- the method is a method of drilling the subterranean formation; or
- the method is a method of fracturing the subterranean formation.

3. The method of claim 1 or claim 2, wherein the composition includes an aqueous liquid, and the method optionally further comprises mixing the aqueous liquid with the polymer viscosifier and the crosslinker.

4. The method of claim 3, wherein the aqueous liquid comprises at least one of water, brine, produced water, flowback water, brackish water, and sea water, the sea water optionally having a total dissolved solids level of about 1,000 mg/L to about 250,000 mg/L or at least about 25,000 mg/L.

5. The method of claim 3 or claim 4, wherein the aqueous liquid comprises at least one of an aqueous drilling fluid and an aqueous fracturing fluid.

6. The method of any one of claims 1 to 5, wherein the crosslinking is at least partially triggered by an increase in temperature, wherein optionally the increase in temperature is at least partially due to placement of the composition in the subterranean formation.

7. The method of claim 6, wherein crosslinking comprises:

- exposing the composition to a temperature of about 150 ºF to about 300 ºF; or
- exposing the composition to a temperature of about 175 ºF to about 250 ºF.

8. The method of any one of claims 1 to 7, wherein after the crosslinking:

- the viscosity of the composition, at standard temperature and pressure and at a shear rate of about 50 s^{-1} to about 500 s^{-1}, is about 10 cP to about 1,000,000 cP;
- the viscosity of the composition, at standard temperature and pressure and at a shear rate of about 0 s^{-1} to about 1 s^{-1}, is about 10 cP to about 1,000,000 cP;
- the viscosity of the composition, at standard temperature and pressure and at a shear rate of about 50 s^{-1} to about 500 s^{-1}, is about 1,000 cP to about 100,000 cP;
- the viscosity of the composition, at standard temperature and pressure and at a shear rate of about 50 s^{-1} to about 500 s^{-1}, is about 0.01 cP to about 1,000,000 cP; or
- the viscosity of the composition, at standard temperature and pressure and at a shear rate of about 50 s^{-1} to about 500 s^{-1}, is about 0.01 cP to about 10,000 cP.

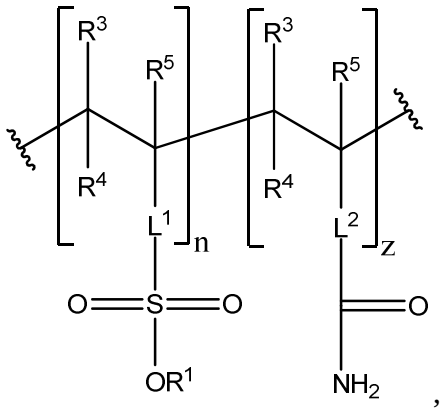
9. The method of any one of claims 1 to 8, wherein:

- about 0.001 wt% to about 95 wt% of the composition is the crosslinkable viscosifier polymer;
- about 70 wt% to about 90 wt% of the composition is the crosslinkable viscosifier polymer;
- about 0.01 wt% to about 50 wt% of the composition is the crosslinkable viscosifier polymer; or
- about 0.01 wt% to about 10 wt% of the composition is the crosslinkable viscosifier polymer.

10. The method of any one of claims 1 to 9, wherein the crosslinkable viscosifier polymer further comprises about M^1 mol% of an ethylene repeating unit comprising a -C(O)OR^1 group, wherein:

- M^1 is about 0% to about 40%;
- M^1 is about 0% to about 20%; or
- $Z^1 + N^1 + M^1$ is about 100%.

11. The method of any one of claims 1 to 10, wherein the crosslinkable viscosifier polymer comprises repeating units having the structure:



,

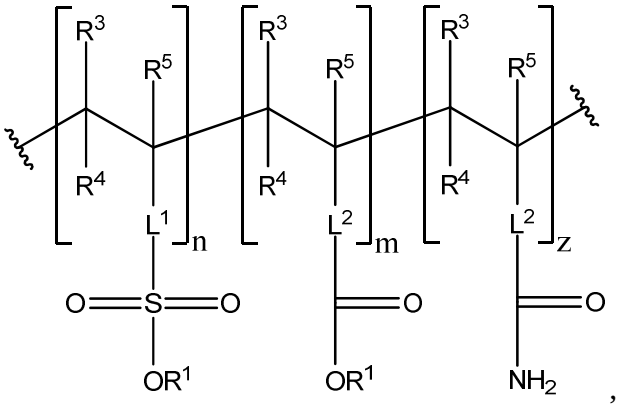
wherein:

at each occurrence R^3, R^4, and R^5 are independently selected from the group consisting of -H and a substituted or unsubstituted C_1-C_5 hydrocarbyl;

at each occurrence L^1 and L^2 are independently selected from the group consisting of a bond and a substituted or unsubstituted C_1-C_{40} hydrocarbyl interrupted or terminated with 0, 1, 2, or 3 of at least one of -NR^3-, -S-, and -O-; and

the repeating units are in a block, alternate, or random configuration, and each repeating unit is independently in the orientation shown or in the opposite orientation.

12. The method of any one of claims 1 to 11, wherein the crosslinkable viscosifier polymer comprises repeating units having the structure:



,

wherein:

at each occurrence R^3, R^4, and R^5 are independently selected from the group consisting of -H and a substituted or unsubstituted C_1-C_5 hydrocarbyl:

at each occurrence L^1 and L^2 are independently selected from the group consisting of a bond and a substituted or unsubstituted C_1-C_{40} hydrocarbyl interrupted or terminated with 0, 1, 2, or 3 of at least one of -NR^3-, -S-, and -O-; and

wherein the repeating units are in a block, alternate, or random configuration, and each repeating unit is independently in the orientation shown or in the opposite orientation.

13. The method of claim 11 or claim 12, wherein at each occurrence:

- L^1 is independently selected from the group consisting of a bond, L^2, and -(substituted or unsubstituted C_1-C_{20} hydrocarbyl)-NR^3-(substituted or unsubstituted C_1-C_{20} hydrocarbyl)-;
- L^1 is independently -C(O)-NH-(substituted or unsubstituted C_1-C_{20} hydrocarbyl)-;

- L^1 is independently -C(O)-NH-(C_1-C_5 hydrocarbyl)-;
- L^1 is -C(O)-NH-CH(CH_3)$_2$-CH_2-.

14. The method of any one of claims 11 to 13, wherein at each occurrence:

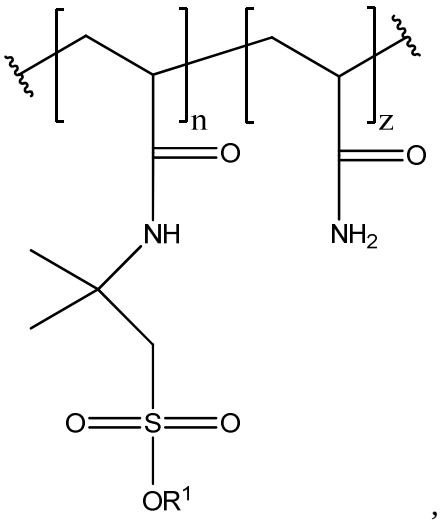
- L^2 is independently selected from the group consisting of a bond and C_1-C_{20} hydrocarbyl;
- L^2 is independently selected from the group consisting of a bond and C_1-C_5 alkyl; or
- L^2 is a bond.

15. The method of any one of claims 11 to 14, wherein at each occurrence:

- R^3, R^4, and R^5 are independently selected from the group consisting of -H and a C_1-C_5 alkyl;
- R^3, R^4, and R^5 are independently selected from the group consisting of -H and a C_1-C_3 alkyl; or
- R^3, R^4, and R^5 are each -H.

16. The method of any one of claims 11 to 15, wherein at each occurrence -R^1 is independently selected from the group consisting of -H, Na^+, K^+, Li^+, NH_4^+, Zn^+, Ca^{2+}, Zn^{2+}, Al^{3+}, and Mg^{2+}.

17. The method of any one of claims 1 to 9, wherein the crosslinkable viscosifier polymer comprises repeating units having the structure:



,

wherein the repeating units are in a block, alternate, or random configuration, and each repeating unit is independently in the orientation shown or in the opposite orientation.

18. The method of any one of claims 1 to 17, wherein:
    - about 0.000,1 wt% to about 80 wt% of the composition is the crosslinker;
    - about 10 wt% to about 30 wt% of the composition is the crosslinker;
    - about 0.000,1 wt% to about 50 wt% of the composition is the crosslinker;
    - about 0.001 wt% to about 1 wt% of the composition is the crosslinker.

19. The method of any one of claims 1 to 18, wherein the crosslinker comprises:
    - at least one of chromium, aluminum, antimony, zirconium, titanium, calcium, boron, iron, silicon, copper, zinc, magnesium, and an ion thereof;
    - at least one of boric acid, borax, a borate, a (C_1-C_{30})hydrocarbylboronic acid, a (C_1-C_{30})hydrocarbyl ester of a (C_1-C_{30})hydrocarbylboronic acid, a (C_1-C_{30})hydrocarbylboronic acid-modified polyacrylamide, ferric chloride, disodium octaborate tetrahydrate, sodium metaborate, sodium diborate, sodium tetraborate, disodium tetraborate, a pentaborate, ulexite, colemanite, magnesium oxide, zirconium lactate, zirconium triethanol amine, zirconium lactate triethanolamine, zirconium carbonate, zirconium acetylacetonate, zirconium malate, zirconium citrate, zirconium diisopropylamine lactate, zirconium glycolate, zirconium triethanol amine glycolate, zirconium lactate glycolate, titanium lactate, titanium malate, titanium citrate, titanium ammonium lactate, titanium triethanolamine, titanium acetylacetonate, aluminum lactate, and aluminum citrate;
    - zirconium or a zirconium derivative; or
    - at least one of zirconium lactate, zirconium triethanol amine, zirconium lactate triethanolamine, zirconium carbonate, zirconium acetylacetonate, zirconium malate, zirconium citrate, zirconium diisopropylamine lactate, zirconium glycolate, zirconium triethanol amine glycolate, and zirconium lactate glycolate.

20. The method of claim 1, wherein the composition further comprises:
    - a fluid comprising at least one of water, an organic solvent, and an oil; or

- a fluid comprising at least one of dipropylene glycol methyl ether, dipropylene glycol dimethyl ether, dimethyl formamide, diethylene glycol methyl ether, ethylene glycol butyl ether, diethylene glycol butyl ether, propylene carbonate, D-limonene, a C_2-C_{40} fatty acid C_1-C_{10} alkyl ester, 2-butoxy ethanol, butyl acetate, furfuryl acetate, dimethyl sulfoxide, dimethyl formamide, diesel, kerosene, mineral oil, a hydrocarbon comprising an internal olefin, a hydrocarbon comprising an alpha olefin, xylenes, an ionic liquid, methyl ethyl ketone, and cyclohexanone.

21. The method of claim 1, wherein the composition further comprises a secondary viscosifier, wherein optionally:

- the secondary viscosifier comprises at least one of a substituted or unsubstituted polysaccharide, and a substituted or unsubstituted polyalkenylene, wherein the substituted or unsubstituted polysaccharide or polyalkenylene is crosslinked or uncrosslinked;
- the secondary viscosifier comprises a polymer comprising at least one monomer selected from the group consisting of ethylene glycol, acrylamide, vinyl acetate, 2-acrylamidomethylpropane sulfonic acid or its salts, trimethylammoniumethyl acrylate halide, and trimethylammoniumethyl methacrylate halide;
- the secondary viscosifier comprises a crosslinked gel or a crosslinkable gel;
- the secondary viscosifier comprises at least one of a linear polysaccharide, and poly((C_2-C_{10})alkenylene), wherein the (C_2-C_{10})alkenylene is substituted or unsubstituted;
- the secondary viscosifier comprises at least one of poly(acrylic acid) or (C_1-C_5)alkyl esters thereof, poly(methacrylic acid) or (C_1-C_5)alkyl esters thereof, poly(vinyl acetate), poly(vinyl alcohol), poly(ethylene glycol), poly(vinyl pyrrolidone), polyacrylamide, poly (hydroxyethyl methacrylate), alginate, chitosan, curdlan, dextran, emulsan, a galactoglucopolysaccharide, gellan, glucuronan, N-acetyl-glucosamine, N-acetyl-heparosan, hyaluronic acid, kefiran, lentinan, levan, mauran, pullulan, scleroglucan, schizophyllan, stewartan, succinoglycan, xanthan, welan, derivatized starch, tamarind, tragacanth, guar

gum, derivatized guar, gum ghatti, gum arabic, locust bean gum, derivatized cellulose, carboxymethyl cellulose, hydroxyethyl cellulose, carboxymethyl hydroxyethyl cellulose, hydroxypropyl cellulose, methyl hydroxyl ethyl cellulose, guar, hydroxypropyl guar, carboxy methyl guar, and carboxymethyl hydroxylpropyl guar;

- the secondary viscosifier comprises poly(vinyl alcohol) homopolymer, poly(vinyl alcohol) copolymer, a crosslinked poly(vinyl alcohol) homopolymer, and a crosslinked poly(vinyl alcohol) copolymer;
- the secondary crosslinker comprises at least one of chromium, aluminum, antimony, zirconium, titanium, calcium, boron, iron, silicon, copper, zinc, magnesium, and an ion thereof; or
- the secondary crosslinker comprises at least one of boric acid, borax, a borate, a (C_1-C_{30})hydrocarbylboronic acid, a (C_1-C_{30})hydrocarbyl ester of a (C_1-C_{30})hydrocarbylboronic acid, a (C_1-C_{30})hydrocarbylboronic acid-modified polyacrylamide, ferric chloride, disodium octaborate tetrahydrate, sodium metaborate, sodium diborate, sodium tetraborate, disodium tetraborate, a pentaborate, ulexite, colemanite, magnesium oxide, zirconium lactate, zirconium triethanol amine, zirconium lactate triethanolamine, zirconium carbonate, zirconium acetylacetonate, zirconium malate, zirconium citrate, zirconium diisopropylamine lactate, zirconium glycolate, zirconium triethanol amine glycolate, zirconium lactate glycolate, titanium lactate, titanium malate, titanium citrate, titanium ammonium lactate, titanium triethanolamine, titanium acetylacetonate, aluminum lactate, and aluminum citrate.

22. The method of any one of claims 1 to 19, further comprising combining the composition, or a crosslinked reaction product thereof, with an aqueous or oil-based fluid comprising a drilling fluid, stimulation fluid, fracturing fluid, spotting fluid, clean-up fluid, completion fluid, remedial treatment fluid, abandonment fluid, pill, acidizing fluid, cementing fluid, packer fluid, or a combination thereof, to form a mixture, wherein the placing the composition in the subterranean formation comprises placing the mixture in the subterranean formation.

23. The method of any one of claims 1 to 22, wherein at least one of prior to, during, and after the placing of the composition in the subterranean formation, the composition, or a crosslinked reaction product thereof, is used downhole, at least one of alone and in combination with other materials, as a drilling fluid, stimulation fluid, fracturing fluid, spotting fluid, clean-up fluid, completion fluid, remedial treatment fluid, abandonment fluid, pill, acidizing fluid, cementing fluid, packer fluid, or a combination thereof.

24. The method of claim 1, wherein the composition further comprises:

- water, saline, aqueous base, oil, organic solvent, synthetic fluid oil phase, aqueous solution, alcohol or polyol, cellulose, starch, alkalinity control agent, acidity control agent, density control agent, density modifier, emulsifier, dispersant, polymeric stabilizer, crosslinking agent, polyacrylamide, polymer or combination of polymers, antioxidant, heat stabilizer, foam control agent, solvent, diluent, plasticizer, filler or inorganic particle, pigment, dye, precipitating agent, rheology modifier, oil-wetting agent, set retarding additive, surfactant, corrosion inhibitor, gas, weight reducing additive, heavy-weight additive, lost circulation material, filtration control additive, salt, fiber, thixotropic additive, breaker, crosslinker, gas, rheology modifier, curing accelerator, curing retarder, pH modifier, chelating agent, scale inhibitor, enzyme, resin, water control material, polymer, oxidizer, a marker, Portland cement, pozzolana cement, gypsum cement, high alumina content cement, slag cement, silica cement, fly ash, metakaolin, shale, zeolite, a crystalline silica compound, amorphous silica, fibers, a hydratable clay, microspheres, pozzolan lime, or a combination thereof; or
- a proppant, a resin-coated proppant, or a combination thereof.

25. The method of claim 1, wherein the placing the composition in a subterranean formation comprises fracturing at least part of the subterranean formation to form at least one subterranean fracture.

26. A system configured to perform the method of any one of claims 1 to 25, the system comprising:

the composition comprising the crosslinkable viscosifier and the crosslinker; and

the subterranean formation comprising the composition therein.

27. The system of claim 26, further comprising

a drillstring disposed in a wellbore, the drillstring comprising a drill bit at a downhole end of the drillstring;

an annulus between the drillstring and the wellbore; and

a pump configured to circulate the composition through the drill string, through the drill bit, and back above-surface through the annulus, and optionally a fluid processing unit configured to process the composition exiting the annulus to generate a cleaned composition for recirculation through the wellbore.