

## THERMALLY EXPANDING SEALING ELEMENTS

### Technical Field

**[0001]** A variety of sealing elements can be used to create a seal within a wellbore or within wellbore tools or equipment. Thermally expanding materials can be included in the sealing elements. The thermally expanding materials can expand with an increase or decrease in temperature. After expansion, the thermally expanding materials can create a better seal than a sealing element without the thermally expanding materials.

### Brief Description of the Figures

**[0002]** The features and advantages of the various embodiments will be more readily appreciated when considered in conjunction with the accompanying figures. The figures are not to be construed as limiting any of the embodiments.

**[0003]** **Fig. 1** is a schematic illustration of a downhole tool including a sealing element according to certain embodiments.

**[0004]** **Fig. 2** is a schematic illustration of a liner hanger including a sealing element according to certain embodiments.

**[0005]** **Fig. 3** is a schematic illustration of a packer assembly including a sealing element according to certain embodiments.

**[0006]** **Fig. 4** is a schematic illustration of expansion of two different thermally expanding materials according to certain embodiments.

### Detailed Description

**[0007]** Oil and gas hydrocarbons are naturally occurring in some subterranean formations. In the oil and gas industry, a subterranean formation containing oil and/or gas is referred to as a reservoir. A reservoir can be located under land or offshore. Reservoirs are typically located in the range of a few hundred feet (shallow reservoirs) to a few tens of thousands of feet (ultra-deep reservoirs). In order to produce oil or gas, a wellbore is drilled into a reservoir or adjacent to a reservoir. The oil, gas, or water produced from a reservoir is called a reservoir fluid.

**[0008]** A well can include, without limitation, an oil, gas, or water production well, an injection well, or a geothermal well. As used herein, a "well" includes at least one wellbore. A wellbore can include vertical, inclined, and horizontal portions, and it can be straight, curved, or branched. As used herein, the term "wellbore" includes any cased, and any uncased, open-hole portion of the wellbore. As used herein, "into a wellbore" means and includes into any portion of the well.

**[0009]** A portion of a wellbore can be an open hole or cased hole. In an open-hole wellbore portion, a tubing string can be placed into the wellbore. The tubing string allows fluids to be introduced into or flowed from a remote portion of the wellbore. In a cased-hole wellbore portion, a casing is placed into the wellbore that can also contain a tubing string. A wellbore can contain an annulus. Examples of an annulus include but are not limited to the space between the wellbore and the outside of a tubing string in an open-hole wellbore, the space between the wellbore and the outside of a casing in a cased-hole wellbore, and the space between the inside of a casing and the outside of a tubing string in a cased-hole wellbore. It is to be understood that reference to a "tubing string" includes a casing string.

**[0010]** A variety of wellbore tools are used in oil and gas operations. The wellbore tools can be run in on a tubing string to perform a variety of functions. The wellbore tools can include one or more sealing elements. By way of a first example, a sealing element can be used to seal one or more components of a downhole tool. Non-limiting examples of downhole tools that utilize sealing elements include sleeves, valves (*e.g.*, flapper valves, safety valves, and barrier valves), and seals for tools that include an interior space that needs to be separated from wellbore fluids, for example, sensors, actuators, telemetry tools, and pressure balancing seals. The sealing element can seal the one or more components of the downhole tools against fluid flow or pressure. Examples of such sealing elements include but are not limited to O-rings, gland seals, stack seals, and gaskets.

**[0011]** During well completion and production, it is commonly desired to seal a portion of an annulus so fluids will not flow through the annulus but rather flow through the tubing string. By sealing the portion of the annulus, oil, gas, water, or combinations thereof can be produced in a controlled manner through the wellhead via the tubing string.

**[0012]** By way of a second example, a sealing element can be used to seal a portion of an annulus. Accordingly, a sealing element can be used in tools that control fluid flow within

an annulus including compression-set packers, expanding packers, and liner hangers. Typically, packers are used to anchor the tubing to the wellbore and to seal the tubing to the wellbore. A packer can be used in cased wellbore portions or open-hole wellbore portions. A packer can include a sealing element that seals to the wellbore to isolate the portion of the wellbore and can also include slips that grip the inside of a tubing string or wall of the wellbore to anchor the packer to the tubing string or wellbore wall. The inner diameter (ID) of the sealing element is positioned around an outer diameter (OD) of an inner mandrel with the ID of the sealing element prevented from disengaging with the OD of the inner mandrel.

**[0013]** Packer sealing elements can be mechanically set, hydraulically set, or hydrostatically set. Other types of packer sealing elements swell in the presence of a setting fluid. As used herein, the term "set" and all grammatical variations thereof means the act of causing or allowing a downhole tool to be permanently or retrievably fixed at a desired location within a wellbore – generally by movement of one or more tool components radially away from an inner mandrel and into contact with an inner diameter of a tubing string or wellbore wall.

**[0014]** Setting of the packer energizes the sealing element to expand away from the outside of the mandrel to engage with the wall of the wellbore or inside of a tubing string. The packer sealing element is constrained on the top and bottom such that during setting, the sealing element is forced outward in a direction away from the mandrel. A mechanical packer uses compression of the tubing string to apply the compressive force needed to energize the element and slips. A hydraulic packer has an internal setting piston that is hydraulically actuated to apply the compression to energize the sealing element and slips. A hydrostatic set packer has an atmospheric chamber that collapses with well hydrostatic pressure to supply the compressive forces needed to set the packer.

**[0015]** All of these types of packers have a sealing element that is a ring of elastomeric material with the entirety of the inner diameter of the sealing element fitted onto the outside of a mandrel. The sealing element is generally constrained on the top and bottom such that actuation of the packer axially squeezes the sealing element to cause radial expansion of the sealing element and seals the annulus. The actuation of the packer deploys the slips to grip and anchor the packer to the inside of the tubing string or wall of the wellbore. For swellable sealing elements, exposure to the setting fluid will cause the sealing element to swell or expand radially away from the inner mandrel to create a seal in the wellbore.

**[0016]** A sealing element can also be used in tools that control fluid flow within a tubing string. By way of a third example, a sealing element can be used to seal a portion of an inside of a tubing string. Plugs, for example bridge plugs, frac plugs, and seals for plug-and-abandonment, can be used to seal an inside of the tubing string. A plug is composed primarily of slips, a plug mandrel, and a rubber sealing element. A plug can be introduced into a wellbore and the sealing element can be caused to block fluid flow into downstream zones when the plug is set much like the sealing element of a packer.

**[0017]** Packers and plugs can be permanent or retrievable. To retrieve a packer or plug, the sealing element can move back radially towards the inner mandrel. In this manner, the sealing element is no longer engaged with the inside of the wellbore wall or tubing string and allows for retrieval from the wellbore, for example with a retrieval tool. For permanent packers or plugs that are not designed to be retrieved from the wellbore, it is not necessary for the sealing element to move back towards the inner mandrel.

**[0018]** A liner hanger is a device used to attach or hang liners from an internal wall of a previous tubing string. The liner hanger's purpose is to suspend a length of liner inside of the previous tubing string while simultaneously sealing the annulus between the liner and the tubing string. The liner hanger can be anchored to the inside of the tubing string by contact between metal ridge located around the outside of the liner hanger and the inside of the tubing string. By way of a fourth example, a sealing element can be used to seal an annulus of a liner hanger.

**[0019]** The bottomhole temperature of a well varies significantly, depending on the subterranean formation and can range from about 100°F to about 600°F (about 37.8°C to about 315.6°C). As used herein, the term "bottomhole" means at the location of the sealing element. Accordingly, the sealing element can encounter a wide range of temperatures within a wellbore. For example, the temperature farther down into a wellbore will generally be greater than the temperature up near the wellhead. Therefore, a downhole tool that is moved to different locations within the wellbore, either farther away from or closer to the wellhead, can encounter wide temperature fluctuations. Moreover, fluids introduced into the wellbore or produced from the wellbore can affect the temperature of wellbore. For example, produced formation fluids generally increase the temperature of the wellbore as the fluids flow up through the tubing string towards the wellhead. When production stops, the wellbore cools back down. Conversely, fluids introduced into the wellbore, for example for carbon sequestration, stimulation treatments,

and secondary recovery operations, generally decrease the temperature of the wellbore as the fluids flow down through the tubing string. When injection of the fluids into the wellbore stops, the wellbore temperature goes back up. It is not uncommon for the temperature within portions of the wellbore to fluctuate 50°C or more. In gas injection wells, such as for carbon sequestration, localized cooling from gas expansion can decrease the ambient bottomhole temperature to -40°C or colder. Steam injection for heavy-oil formations for example can inject fluids that are 400°C hotter than the ambient bottomhole temperature.

**[0020]** Most sealing elements are made from an elastomer material that is capable of elastically stretching and can impart structural integrity to the seal created. However, wide temperature fluctuations can decrease the structural integrity of the sealing element by causing small gaps or cracks in the elastomer material to form or by decreasing the elastic strain in the elastomer material or by decreasing the tensile strength of the elastomer material—especially at the interface between the sealing element and the tool component, wellbore wall, or tubing string. This can compromise the seal whereby pressure is no longer maintained and/or fluid can bypass the seal.

**[0021]** Some attempts to solve this problem include using seal stacks, which are multiple sealing elements located adjacent to each other. However, not only is the use of multiple sealing elements expensive, but also the dimensions of the downhole tool must be increased in order to accommodate the multiple sealing elements. Thus, there is a need for sealing elements that can maintain structural integrity in environments with wide temperature fluctuations.

**[0022]** It has been discovered that a sealing element can include a substance that expands during or after a phase change. An expanding substance can maintain structural integrity of the sealing element during temperature fluctuations. An expanding substance included in the sealing element can fill imperfections in the tubing string, increase the contact stresses against the tubing string or downhole tool components, and increase the seal and anchor performance. The additional expansion from the phase change substance can also help to overcome the elastic recoil from the expansion process. As used herein, the term "expand," "expansion," and all grammatical variations thereof means an increase in the volume of the substance. As used herein, a "phase change" means any change that occurs to the physical properties of the substance. As used herein, a "phase change" can include, without limitation, a

change in the phase of the substance (*i.e.*, from a solid to a liquid or semi-liquid, from a liquid or semi-liquid to a solid, from a liquid or semi-liquid to a gas, *etc.*), a glass transition, a change in the amount of crystallinity of the substance, physical changes to the amorphous and/or crystalline portions of the substance, and any combinations thereof. A substance will undergo a phase change at a "phase change temperature." As used herein, a "phase change temperature" includes a single temperature and a range of temperatures at which the substance undergoes a phase change. The "phase change temperature" can be the single temperature or range of temperatures in which the largest volume expansion occurs. Therefore, it is not necessary to continually specify that the phase change temperature can be a single temperature or a range of temperatures throughout. A material may have multiple phase change temperatures corresponding to the phase change of different constituents within the material.

**[0023]** According to any of the embodiments, a well system comprising: a wellbore that penetrates a subterranean formation; and a sealing element comprising: an elastomer matrix; and a substance embedded within the elastomer matrix, wherein the substance expands at a phase change temperature.

**[0024]** According to any of the embodiments, a method of creating a seal within a wellbore comprises: introducing a downhole tool into the wellbore, wherein the downhole tool comprises a sealing element, wherein the sealing element comprises: an elastomer matrix; and a substance embedded within the elastomer matrix, wherein the substance expands at a phase change temperature; and causing or allowing the sealing element to create the seal within the wellbore.

**[0025]** The various disclosed embodiments apply to the systems, methods, and apparatuses without the need to repeat the various embodiments throughout. As used herein, any reference to the unit "gallons" means U.S. gallons.

**[0026]** The well system includes a sealing element. The sealing element can be located on a downhole tool. The downhole tool can be, for example, sleeves, valves (*e.g.*, safety valves and barrier valves), and seals for tools that include an interior space that needs to be separated from wellbore fluids, for example, sensors, actuators, telemetry tools, and pressure balancing seals, a packer assembly, a plug, or a liner hanger.

**[0027]** The sealing element can be any type of element that creates a seal between two components. By way of a first example, the sealing element can create a seal between two

components of a downhole tool. According to this example, the sealing element can be without limitation an O-ring, gland seal, stack seal, or gasket. Turning to the Figures, **Fig. 1** is a schematic illustration of a downhole tool including a sealing element. It is to be understood that the downhole tool shown in **Fig. 1** is just one example of a downhole tool that can include a sealing element as other downhole tools not shown can include the sealing element. The downhole tool can include a body **213**. The body **213** can be configured to fit within a tubing string **112**. The tubing string **112** and the downhole tool can be introduced into a wellbore that is defined by a wellbore wall **120**. An annulus can be defined as the space located between the wellbore wall **120** and the outside of the tubing string **112** and body **213**.

[0028] The downhole tool can include an inner sleeve **130** and a housing **160**. The inner sleeve **130** can be releasably attached to the housing **160** by a frangible device **147**. The downhole tool can also include a valve **141**. The valve **141** can be, for example, a flapper valve. The inner sleeve **130** and the housing **160** can also include one or more lock rings **133**. The downhole tool also includes a sealing element **134** that restricts or prevents fluid flow between two or more tool components. By way of example and as shown in **Fig. 1**, the sealing element **134** can restrict or prevent fluid flow between the outside of the inner sleeve **130** and the inside of the housing **160**.

[0029] By way of another example, the sealing element can create a seal between the outside of a mandrel of the downhole tool and the inside of a wall of the wellbore or the inside of a tubing string. According to this example, the downhole tool can be a packer assembly, a liner hanger, or a plug, and the sealing element can be located around the outside of the mandrel of the packer assembly or the plug.

[0030] **Fig. 2** shows an example of a liner hanger including a sealing element. A tubing system can function as a conduit for a wellbore that penetrates a subterranean formation **102**. The tubing system can include a surface casing **20** and a surface cement sheath **25** that anchors the surface casing **20** in the wellbore. The surface casing **20** can extend from the surface **30** down to a desired depth in the well. An intermediate casing **35** can be deployed concentrically within the surface casing **20**. The intermediate casing **35** can be held in place within the surface casing **20** with an intermediate cement sheath **40**. Multiple layers of intermediate casings can be used. A liner hanger **45** is deployed within the intermediate casing **35**. The liner hanger **45** can suspend a liner **55** from its end. The liner hanger **45** can be

anchored to the intermediate casing **35** with a series of sealing elements **50**. The sealing elements **50** can seal an annulus located between the outside of an inner intermediate casing and the inside of the adjacent intermediate casing. The seal can inhibit or prevent wellbore fluids from bypassing the liner **55** and liner hanger **45**.

**[0031]** The downhole tool can also be a packer. **Fig. 3** shows the well during a fracturing operation in a portion of a subterranean formation **102**. The subterranean formation **102** can be penetrated by a well. The well includes a wellbore **104**. The wellbore **104** extends from the surface **106**, and a fracturing fluid **108** is introduced into a portion of the subterranean formation **102**. A pump and blender system **100** can be coupled to a tubing string **112** to pump the fracturing fluid **108** into the wellbore **104** to create one or more fractures **116** in the subterranean formation **102**. The wellbore **104** can include a casing **110** that is cemented or otherwise secured to the wellbore wall. The wellbore **104** can be uncased or include uncased sections. Perforations can be formed in the casing **110** or tubing string **112** to allow fracturing fluids and/or other materials to flow into the subterranean formation **102**. The well system can include one or more sets of packers **114** that create one or more wellbore intervals. The packers **114** include a sealing element **118** located around the outside of the packers. The sealing element **118** can seal an annulus located between the outside of a tubing string **112** and the wellbore wall **120**.

**[0032]** There can also be more than one sealing element located on the downhole tool. For example, a sleeve can include an O-ring and a gasket located at different positions on the downhole tool. More than one downhole tool (*e.g.*, a packer assembly and a sleeve) can also include at least one sealing element.

**[0033]** The sealing element includes an elastomer matrix. As used herein, the term "elastomer" means a natural or synthetic polymer having elastic properties. As used herein, the term "matrix" means a surrounding medium or structure. The elastomer of the matrix can be the material in the greatest concentration of the sealing element and can provide the necessary structure in which a substance can be embedded within the matrix.

**[0034]** Polymers commonly include amorphous regions and crystalline regions. A polymer is a large molecule composed of repeating units, typically connected by covalent chemical bonds. A polymer is formed from monomers. During the formation of the polymer, some chemical groups can be lost from each monomer. The piece of the monomer that is

incorporated into the polymer is known as the repeating unit or monomer residue. The backbone of the polymer is the continuous link between the monomer residues. The polymer can also contain functional groups or side chains connected to the backbone at various locations along the backbone. Polymer nomenclature is generally based upon the type of monomer residues comprising the polymer. A polymer formed from one type of monomer residue is called a homopolymer. A copolymer is formed from two or more different types of monomer residues. The number of repeating units of a polymer is referred to as the chain length of the polymer. The number of repeating units of a polymer can range from approximately 11 to greater than 10,000. In a copolymer, the repeating units from each of the monomer residues can be arranged in various manners along the polymer chain. For example, the repeating units can be random, alternating, periodic, or block. The conditions of the polymerization reaction can be adjusted to help control the average number of repeating units (the average chain length) of the polymer. As used herein, a "polymer" can include a cross-linked polymer. As used herein, a "cross link" or "cross linking" is a connection between two or more polymer molecules. A cross-link between two or more polymer molecules can be formed by a direct interaction between the polymer molecules, or conventionally, by using a cross-linking agent that reacts with the polymer molecules to link the polymer molecules.

**[0035]** A polymer has an average molecular weight, which is directly related to the average chain length of the polymer. For a copolymer, each of the monomers will be repeated a certain number of times (number of repeating units). The average molecular weight for a copolymer can be expressed as follows:

$$\text{Avg. molecular weight} = (\text{M.W.}_{m_1} * \text{RU } m_1) + (\text{M.W.}_{m_2} * \text{RU } m_2) \dots$$

where  $\text{M.W.}_{m_1}$  is the molecular weight of the first monomer;  $\text{RU } m_1$  is the number of repeating units of the first monomer;  $\text{M.W.}_{m_2}$  is the molecular weight of the second monomer; and  $\text{RU } m_2$  is the number of repeating units of the second monomer. Of course, a terpolymer would include three monomers, a tetra polymer would include four monomers, and so on.

**[0036]** The elastomer can be a non-reactive polymer, a degradable polymer, or a polymer that swells in the presence of a fluid, for example, a water-based fluid or an oil-based fluid. Non-limiting examples of non-reactive polymers include nitrile rubber, hydrogenated

nitrile rubber (HNBR), a fluorocarbon-based fluoroelastomer rubber containing vinylidene fluoride as a monomer such as FKM or FFKM rubbers, natural rubber, polyetheretherketone rubbers (PEEK), and polytetrafluoroethylene (PTFE), which is a synthetic fluoropolymer of tetrafluoroethylene sold under the brand name TEFLON®.

**[0037]** Degradable polymers include polymers that dissolve in a wellbore fluid. Non-limiting examples of degradable polymers include urethane, polyurethane rubber, polyether-based rubber, polyester-based rubber, polylactic acid-based polymers, polyglycolic acid-based polymers, polyvinyl alcohol-based polymers, and thiol-based polymers.

**[0038]** Non-limiting examples of swellable polymers include EPDM and rubbers that are made with super absorbent additives (SAP). EPDM is a copolymer made from ethylene, propylene, and diene co-monomers that enable crosslinking via sulfur vulcanization. Dienes used in the manufacture of EPDM rubbers are ethylidene norbornene (ENB), dicyclopentadiene (DCPD), and vinyl norbornene (VNB). EPDM is derived from polyethylene into which 45-85 wt% of propylene has been copolymerized to reduce the formation of the typical polyethylene crystallinity. EPDM is a semi-crystalline material with ethylene-type crystal structures at higher ethylene contents, becoming essentially amorphous at ethylene contents that approach 50 wt%.

**[0039]** The elastomer matrix polymer can also include more than one type of polymer, such as a thermoplastic or thermoset elastomer. Examples of a thermoplastic elastomer include thermoplastic urethane, block copolymers, thermoplastic olefins, and thermoplastic polyamides. According to a first embodiment, the polymer is a thermoset elastomer in which the sealing element is formed from a cast. According to another embodiment, the polymer is a thermoplastic polymer in which the sealing element is molded.

**[0040]** The sealing element can be axially constrained on the top and/or bottom such that the sealing element expands in a radial direction only, for example when the sealing element is included in a packer assembly or plug. The sealing element can also be constrained around the outside of the element such that the sealing element expands laterally up and down, for example when the sealing element is an O-ring or gasket. After expansion, the sealing element can create a seal between two or more wellbore components. The elastomer matrix can be energized through mechanical compression, and according to some of the embodiments, does not require an application of pressure to create a seal. According to any of the embodiments, the sealing element creates a seal through compression of the sealing element between two surfaces with

compressive loads exceeding 500 pounds force per square inch (psi) for example. The seal created can form a bi-directional seal wherein the sealing element can hold pressure in two directions, for example above and below the seal. According to any of the embodiments, the sealing element is capable of bi-directionally holding pressures up to 500 psi or greater.

**[0041]** As discussed above, when elastomer sealing elements encounter large temperature fluctuations (*i.e.*, +/- 50°C), small cracks or voids can develop in the sealing element and negatively affect the integrity of the seal created. By way of example, when a sealing element is tested at a high temperature and then placed in a location having a lower temperature, the elastomer seems to "take a set" at the high temperature and has trouble returning to size when cooled. Conversely, elastomers tested at a lower temperature can lose sealing capability when placed in a location having a higher temperature.

**[0042]** The sealing element also includes a substance embedded within the elastomer matrix, wherein the substance expands at a phase change temperature. The substance expands in volume. The expansion in volume can occur in one or more dimensions. It is to be understood that unlike a swellable elastomer that swells in the presence of a fluid, the substance expands in response to temperature and does not expand or swell in the presence of a fluid. The response and subsequent expansion of the substance can be nearly instantaneous when the substance passes through the phase change temperature, for example within seconds or minutes. The expansion of the substance can counteract the negative effects of large temperature fluctuations. Other advantages to the expansion of the substance embedded within the elastomer matrix include, but are not limited to, overcoming compression set in the sealing element or overcoming elastic recoil in the movement of a mandrel supporting the elastomer matrix, such as the elastic recoil from expanding a liner hanger.

**[0043]** The phase change temperature can be greater than or less than the temperature at the wellhead. According to any of the embodiments, the substance expands with an increase in temperature at or above the phase change temperature. As used herein, the phrase "expands with an increase in temperature" means a material that expands by more than 5% in volume as it experiences a phase change from a lower temperature to a higher temperature. The phase change according to these embodiments can be a solid/liquid, solid/semi-liquid, and glass transition. The substance can be an organic-based substance. The organic-based substance can be amorphous or semi-crystalline in structure. The organic-based substance can be a polymeric

plastic or a thermoplastic including acrylonitrile butadiene styrene (ABS), polypropylene, nylon 6/6, acetal, polycarbonate, or polyester. A semi-crystalline organic-based substance can be, for example, high-density polyethylene (HDPE). The organic-based substance can be a wax. The wax can be, for example, a paraffin wax or an animal or plant fat, such as stearic acid. The phase change temperature for organic-based substances can differ. By way of example, the phase change temperature for paraffin wax can be in the range of 0°C to 150°C depending on the composition of the paraffin wax and additional constituents within the wax, while the phase change temperature for stearic acid wax can be 70°C, while the phase change temperature for HDPE can be 125°C. The sealing element can also include more than one type of organic-based substance, each substance having a different phase change temperature, in order to cover a broader range of bottomhole temperatures. By way of example, the organic-based substance can include paraffin wax and stearic acid. **Table 1** lists non-limiting examples of volume expansion of different organic-based substances with an increase in temperature.

| Composition   | Volume Expansion (%) |
|---------------|----------------------|
| Paraffin      | 15                   |
| Stearic acid  | 10                   |
| ABS           | 12                   |
| Polypropylene | 28                   |
| Nylon 6/6     | 18                   |
| Acetal        | 21                   |
| Polycarbonate | 18                   |
| Polyester     | 21                   |
| HDPE          | 25                   |

**Table 1**

**[0044]** According to any of the embodiments, the substance expands with a decrease in temperature at or below the phase change temperature. As used herein, the phrase "expands with a decrease in temperature" means a material that expands by more than 0.5% in volume as it experiences a phase change from a higher temperature to a lower temperature. **Fig. 4** is an illustration of volumetric expansion of paraffin with an increase in temperature and a bismuth alloy with a decrease in temperature. The phase change temperature according to these embodiments can be the freezing point of the substance. The phase change according to these embodiments can be a liquid/solid or semi-liquid/solid. The substance can be a metal-based

substance, for example a pure metal or a metal alloy. As used herein, the term "metal alloy" means a mixture of two or more elements, wherein at least one of the elements is a metal. The other element(s) can be a non-metal or a different metal. An example of a metal and non-metal alloy is steel, comprising the metal element iron and the non-metal element carbon. An example of a metal and metal alloy is bronze, comprising the metallic elements copper and tin. Examples of suitable metals for the metal-based substance include, but are not limited to, any pure metals or metal alloys of bismuth, gallium, germanium, or any combination thereof. The metal-based substance may be alloyed with other elements to promote mechanical properties or to adjust the phase change temperature. Alloying elements include silicon, antimony, tin, lead, cadmium, indium, magnesium, manganese, zinc, thallium, mercury, lithium, sodium, and potassium. Properties of different metals and metal alloys are shown in **Table 2** with volume expansion with a decrease in temperature.

| Composition                     | Freezing Point (°C) | Volume Expansion (%) | Tensile Strength (psi) |
|---------------------------------|---------------------|----------------------|------------------------|
| 100%Ga                          | 29                  | 3.1                  | 2,100                  |
| 45%Bi; 23%Pb; 8%Sn; 5%Cd; 19%In | 47                  | 1.4                  | 5,400                  |
| 43%Bi; 38%Pb; 11%Sn; 9%Cd       | 71 – 88             | 2.0                  | 5,400                  |
| 48%Bi; 28%Pb; 15%Sn, 9%Sb       | 103 – 226           | 1.5                  | 13,000                 |
| 55%Bi; 45%Pb                    | 124                 | 1.5                  | 6,400                  |
| 100%Bi                          | 271                 | 3.3%                 | 2,900                  |

**Table 2**

**[0045]** The substance can be selected based on the phase change temperature of that substance and the anticipated bottomhole temperature increase or decrease. By way of example, if formation fluids are to be produced and the bottomhole temperature is anticipated to increase to 200°C during production, then an organic-based substance having a phase change temperature of at least 100°C, HDPE for example, can be selected. In this manner, when the bottomhole temperature increases to the phase change temperature of the substance, the substance will undergo the phase change and expand. By way of another example, if fluids are to be injected into the wellbore and the bottomhole temperature is anticipated to decrease to 30°C, then a metal-based substance having a phase change temperature of less than or equal 30°C, pure metal gallium for example, can be selected.

**[0046]** According to certain embodiments, one or more substance – each of which having a phase change above or below their phase change temperature – can be used to cover a wide range of bottomhole temperature changes. For example, one or more metal-based substances can be selected, wherein each substance undergoes a phase change at or below the freezing point and each substance has a different phase change temperature. By way of another example, one or more organic-based substances can be selected, wherein each substance undergoes a phase change at or above the melting point and each substance has a different phase change temperature. These embodiments can be useful when the sealing element is included on a downhole tool that is to be retrieved from the wellbore after use (*e.g.*, packers or plugs). In this manner, when the bottomhole temperature increases or decreases (for example during production or injection) the substance can expand and provide a better seal. Then, when the bottomhole temperature reverts back (for example after production or injection stops), then the substance can contract and no longer be in sealing engagement with tool components, the wall of the wellbore, or the inside of a tubing string. In this manner, the downhole tool can be retrieved.

**[0047]** According to certain other embodiments, two or more substances – one having a phase change above its phase change temperature and the other having a phase change below its phase change temperature – can be used to cover a wide range of bottomhole temperature changes. For example, at least one metal-based substance can be selected and at least one organic-based substance can be selected. These embodiments can be useful when the sealing element is included on a downhole tool that is to permanently remain in the wellbore after use (*e.g.*, permanent packers or plugs). These embodiments can also be useful when the seal created is between components of the downhole tool and the downhole tool is retrievable (*e.g.*, O-rings or gaskets). In this manner, when the bottomhole temperature increases (for example during production) the organic-based substance can expand and provide a better seal. Then, when the bottomhole temperature cools back down (for example during injection), then the metal-based substance can expand and still provide a better seal.

**[0048]** The volume expansion of the substance can be different for different substances. According to any of the embodiments, the substance is selected such that the substance expands at least 1%, 3%, or 15% in volume. The volume expansion of organic-based substances is generally greater than metal-based substances as seen in **Tables 1 and 2**.

**[0049]** Prior to the phase change, the sealing capability of the sealing element can be diminished, for example, due to temperature fluctuations during wellbore operations that create small gaps around and/or throughout the sealing element. According to any of the embodiments, the substance expands a sufficient volume such that any small gaps created on the sealing element from temperature fluctuations are filled with the substance. Accordingly, after expansion from the phase change, the sealing capability of the sealing element can be restored. The sealing capability can be restored such that the sealing element is capable of withstanding a desired pressure differential. The pressure differential can be the bottomhole pressure of the subterranean formation across the sealing element. After the substance undergoes a phase change, then the strength of the sealing element can increase. By way of example, the bulk modulus of paraffin is roughly 240,000 psi, which indicates that the expanding organic-based substance can exert significant force on components and thus strengthen the sealing element.

**[0050]** The substance can be in the form of particles. The particles can have a variety of geometric shapes, such as generally spherical, acicular, or cuboid, and can have generally smooth or jagged perimeters. The size of the particles can vary and can range from 10 millimeters (mm) to 1,000 nanometers (nm). The particle size can be in the range of 1 mm to 10 nm. The particles are embedded within the elastomer matrix. The particles can be interspersed throughout the elastomer matrix. The particles can also be embedded at one or more select regions of the elastomer matrix, for example just around the outer perimeter of the elastomer matrix, where small gaps or cracks are most likely to form due to temperature fluctuations.

**[0051]** The sealing element can be located on the downhole tool adjacent to a second sealing element that does not include the substance. This embodiment can be useful if the substance reduces the overall strength of the sealing element. In this manner, the use of a second sealing element can ensure adequate seals are created.

**[0052]** The substance particles can also include other materials in addition to the phase change substance. For example, non-reactive strengtheners can be added to the organic-based substance. Fibers or other particles can be used to increase the stiffness of the metal-based substance. The concentration of other materials can be selected such that the sealing capabilities of the sealing element are maintained after the phase change. For example, including other materials at a higher concentration reduces the amount of the phase change substance that is available for expansion.

**[0053]** There is a potential for some waxes to seep out of the elastomer matrix at high temperatures. If the wax seeps out of the elastomer matrix, then the wax would no longer provide long-term sealing enhancement from expanding. According to any of the embodiments, the organic-based substance particles are encapsulated in a shell. The shell can be used to keep the wax as a distinct phase within the elastomer matrix. The materials for the shell can be oil incompatible so the shell material does not seep out the elastomer matrix. The shell material can stretch. In this manner, when the substance expands during the phase change, the shell will not crack and provide a path for the substance to seep out of the elastomer matrix. The shell material can be selected from polymeric materials comprising acrylic, epoxy, silver, polystyrene, carbon nanotubes, silicon dioxide, fluorocarbon-based fluoroelastomer (FKM), or polytetrafluoroethylene (PTFE), which is a synthetic fluoropolymer of tetrafluoroethylene sold under the brand name TEFLON®.

**[0054]** The methods include introducing the downhole tool within the wellbore. The well can be, without limitation, an oil, gas, or water production well, an injection well, or a geothermal well. The well can also be an offshore well. The methods can include causing or allowing the bottomhole temperature of the wellbore to decrease. The decrease in temperature can be performed after the downhole tool is introduced within the wellbore. The step of decreasing can include introducing a fluid into the wellbore or cessation of producing formation fluids. The fluid can be a variety of types of fluids used in oil or gas operations, for example, drilling fluids, injection fluids, fracturing fluids, work-over fluids, acidizing fluids, gravel packing fluids, completion fluids, and stimulation fluids. According to this embodiment, the fluid being introduced into the wellbore has a surface temperature that is less than the phase change temperature of the substance. By way of example, fracturing fluids can cool the bottomhole temperature of the wellbore by over 100°F (37.8°C). The temperature of the portion of the wellbore can be decreased to a temperature that is less than or equal to the phase transition temperature of the metal-based substance.

**[0055]** The methods include causing or allowing the bottomhole temperature of the wellbore to increase. The bottomhole temperature can be increased by introducing a fluid into the wellbore, producing a fluid from the wellbore, or cessation of pumping a colder fluid into the wellbore. The fluid can have a temperature greater than or equal to the phase change temperature of the substance. According to any of the embodiments, the phase change of the

substance occurs within the normal operating bottomhole temperatures encountered during the oil or gas operation. Normal operating bottomhole temperatures encountered can range from -40°C to 550°C or from 4°C to 200°C depending on the specific oil or gas operation performed.

**[0056]** The following are two, non-limiting examples of uses of the sealing element with a metal-based substance that expands when the temperature decreases below the phase change temperature. According to a first example, the sealing element is placed on the outside of a casing. The heat of curing cement located in an annulus between the casing and the wall of the wellbore causes the phase-change of the metal from a solid to a liquid, which results in the contraction of the metal-based substance, and consequently a reduced volume of the elastomer matrix, which allows more cement to fill the annular gap. After the curing is complete and the bottomhole temperature decreases, the metal-based phase-change material expands and helps to seal any potential annular gaps between the casing and the cement. According to a second example, the sealing element is part of a frac plug. The wellbore is warm when the plug is installed, and the metal-based substance is liquid, which allows for a low setting force. During a fracturing operation, the injected water cools the frac plug and solidifies the metal-based substance. The metal expands as it solidifies and enhances the seal. The solidified metal also increases the stiffness of the elastomer matrix, which increases the pressure holding capability of the plug.

**[0057]** The following are two, non-limiting example of uses of the sealing element with an organic-based substance that expands when the temperature increases above the phase change temperature. According to a first example, a packer including the sealing element is introduced into a geothermal well. The organic-based substance is solid when set. As hot water is produced from the geothermal wellbore, the organic-based substance expands and increases the integrity and pressure holding capability of the seal. According to a second example, a liner hanger includes the organic-based substance in at least one of the sealing elements. The liner hanger is expanded into position and set to seal between the outside of a tubing string and the inside of another tubing string. As the subterranean formation heats up the sealing element, the organic-based substance expands and helps to overcome any elastic recoil that may have occurred during the setting of the liner hanger.

**[0058]** An embodiment of the present disclosure is a well system comprising: a wellbore that penetrates a subterranean formation; and a downhole tool comprising a sealing

element, wherein the sealing element comprises: an elastomer matrix; and a substance embedded within the elastomer matrix, wherein the substance expands at a phase change temperature. Optionally, the well system further comprises wherein the downhole tool is selected from a sleeve, a valve, a sensor, an actuator, a telemetry tool, a pressure balancing seal, a packer assembly, a plug, or a liner hanger. Optionally, the well system further comprises wherein the sealing element creates a seal between components of the downhole tool, and wherein the sealing element is an O-ring, gland seal, stack seal, or gasket. Optionally, the well system further comprises wherein the sealing element creates a seal between an outside of a mandrel of the downhole tool and the inside of a wall of the wellbore or the inside of a tubing string, and wherein the downhole tool is a packer assembly, a liner hanger, or a plug. Optionally, the well system further comprises wherein the elastomer of the elastomer matrix is a non-reactive polymer, a degradable polymer, or a polymer that swells in the presence of a fluid. Optionally, the well system further comprises wherein the substance expands with an increase in temperature at or above the phase change temperature. Optionally, the well system further comprises wherein the substance is an organic-based substance. Optionally, the well system further comprises wherein the organic-based substance is selected from the group consisting of: a polymeric plastic; a thermoplastic comprising acrylonitrile butadiene styrene, polypropylene, nylon 6/6, acetal, polycarbonate, or polyester; a semi-crystalline organic-based substance; or a wax comprising paraffin or stearic acid. Optionally, the well system further comprises wherein the sealing element further comprises a second organic-based substance, wherein the second organic-based substance has a different phase change temperature than the organic-based substance. Optionally, the well system further comprises wherein the organic-based substance is in the form of particles, and wherein the particles are encapsulated in a shell. Optionally, the well system further comprises wherein the substance expands with a decrease in temperature at or below the phase change temperature. Optionally, the well system further comprises wherein the substance is a metal-based substance. Optionally, the well system further comprises wherein the metal-based substance comprises pure metals or metal alloys comprising bismuth, gallium, germanium, silicon, antimony, tin, lead, cadmium, indium, magnesium, manganese, zinc, thallium, mercury, lithium, sodium, potassium, and combinations thereof. Optionally, the well system further comprises wherein the sealing element further comprises a second metal-based substance, wherein the second metal-based substance has a different phase change temperature

than the metal-based substance. Optionally, the well system further comprises wherein the substance expands with an increase in temperature at or above the phase change temperature, and wherein the sealing element further comprises a second substance, wherein the second substance expands with a decrease in temperature at or below the phase change temperature. Optionally, the well system further comprises wherein the substance is selected such that the substance expands at least 1% in volume. Optionally, the well system further comprises wherein the substance is in the form of particles having a particle size in the range of 10 millimeters to 1,000 nanometers. Optionally, the well system further comprises wherein the particles are interspersed throughout the elastomer matrix.

**[0059]** Another embodiment of the present disclosure is a method of creating a seal within a wellbore comprising: introducing a downhole tool into the wellbore, wherein the downhole tool comprises a sealing element, wherein the sealing element comprises: an elastomer matrix; and a substance embedded within the elastomer matrix, wherein the substance expands at a phase change temperature; and causing or allowing the sealing element to create the seal within the wellbore. Optionally, the method further comprises wherein the downhole tool is selected from a sleeve, a valve, a sensor, an actuator, a telemetry tool, a pressure balancing seal, a packer assembly, a plug, or a liner hanger. Optionally, the method further comprises wherein the sealing element creates a seal between components of the downhole tool, and wherein the sealing element is an O-ring, gland seal, stack seal, or gasket. Optionally, the method further comprises wherein the sealing element creates a seal between an outside of a mandrel of the downhole tool and the inside of a wall of the wellbore or the inside of a tubing string, and wherein the downhole tool is a packer assembly, a liner hanger, or a plug. Optionally, the method further comprises wherein the elastomer of the elastomer matrix is a non-reactive polymer, a degradable polymer, or a polymer that swells in the presence of a fluid. Optionally, the method further comprises wherein the substance expands with an increase in temperature at or above the phase change temperature. Optionally, the method further comprises wherein the substance is an organic-based substance. Optionally, the method further comprises wherein the organic-based substance is selected from the group consisting of: a polymeric plastic; a thermoplastic comprising acrylonitrile butadiene styrene, polypropylene, nylon 6/6, acetal, polycarbonate, or polyester; a semi-crystalline organic-based substance; or a wax comprising paraffin or stearic acid. Optionally, the method further comprises wherein the sealing element further comprises a second

organic-based substance, wherein the second organic-based substance has a different phase change temperature than the organic-based substance. Optionally, the method further comprises wherein the organic-based substance is in the form of particles, and wherein the particles are encapsulated in a shell. Optionally, the method further comprises wherein the substance expands with a decrease in temperature at or below the phase change temperature. Optionally, the method further comprises wherein the substance is a metal-based substance. Optionally, the method further comprises wherein the metal-based substance comprises pure metals or metal alloys comprising bismuth, gallium, germanium, silicon, antimony, tin, lead, cadmium, indium, magnesium, manganese, zinc, thallium, mercury, lithium, sodium, potassium, and combinations thereof. Optionally, the method further comprises wherein the sealing element further comprises a second metal-based substance, wherein the second metal-based substance has a different phase change temperature than the metal-based substance. Optionally, the method further comprises wherein the substance expands with an increase in temperature at or above the phase change temperature, and wherein the sealing element further comprises a second substance, wherein the second substance expands with a decrease in temperature at or below the phase change temperature. Optionally, the method further comprises wherein the substance is selected such that the substance expands at least 1% in volume. Optionally, the method further comprises wherein the substance is in the form of particles having a particle size in the range of 10 millimeters to 1,000 nanometers. Optionally, the method further comprises wherein the particles are interspersed throughout the elastomer matrix.

**[0060]** Another embodiment of the present disclosure is a downhole tool comprising: a mandrel; and a sealing element located adjacent to the mandrel, wherein the sealing element comprises: an elastomer matrix; and a substance embedded within the elastomer matrix, wherein the substance expands at a phase change temperature. Optionally, the downhole tool further comprises wherein the downhole tool is selected from a sleeve, a valve, a sensor, an actuator, a telemetry tool, a pressure balancing seal, a packer assembly, a plug, or a liner hanger. Optionally, the downhole tool further comprises wherein the sealing element creates a seal between components of the downhole tool, and wherein the sealing element is an O-ring, gland seal, stack seal, or gasket. Optionally, the downhole tool further comprises wherein the sealing element creates a seal between an outside of a mandrel of the downhole tool and the inside of a wall of the wellbore or the inside of a tubing string, and wherein the downhole tool is a packer

assembly, a liner hanger, or a plug. Optionally, the downhole tool further comprises wherein the elastomer of the elastomer matrix is a non-reactive polymer, a degradable polymer, or a polymer that swells in the presence of a fluid. Optionally, the downhole tool further comprises wherein the substance expands with an increase in temperature at or above the phase change temperature. Optionally, the downhole tool further comprises wherein the substance is an organic-based substance. Optionally, the downhole tool further comprises wherein the organic-based substance is selected from the group consisting of: a polymeric plastic; a thermoplastic comprising acrylonitrile butadiene styrene, polypropylene, nylon 6/6, acetal, polycarbonate, or polyester; a semi-crystalline organic-based substance; or a wax comprising paraffin or stearic acid. Optionally, the downhole tool further comprises wherein the sealing element further comprises a second organic-based substance, wherein the second organic-based substance has a different phase change temperature than the organic-based substance. Optionally, the downhole tool further comprises wherein the organic-based substance is in the form of particles, and wherein the particles are encapsulated in a shell. Optionally, the downhole tool further comprises wherein the substance expands with a decrease in temperature at or below the phase change temperature. Optionally, the downhole tool further comprises wherein the substance is a metal-based substance. Optionally, the downhole tool further comprises wherein the metal-based substance comprises pure metals or metal alloys comprising bismuth, gallium, germanium, silicon, antimony, tin, lead, cadmium, indium, magnesium, manganese, zinc, thallium, mercury, lithium, sodium, potassium, and combinations thereof. Optionally, the downhole tool further comprises wherein the sealing element further comprises a second metal-based substance, wherein the second metal-based substance has a different phase change temperature than the metal-based substance. Optionally, the downhole tool further comprises wherein the substance expands with an increase in temperature at or above the phase change temperature, and wherein the sealing element further comprises a second substance, wherein the second substance expands with a decrease in temperature at or below the phase change temperature. Optionally, the downhole tool further comprises wherein the substance is selected such that the substance expands at least 1% in volume. Optionally, the downhole tool further comprises wherein the substance is in the form of particles having a particle size in the range of 10 millimeters to 1,000 nanometers. Optionally, the downhole tool further comprises wherein the particles are interspersed throughout the elastomer matrix.

[0061] Therefore, the various embodiments are well adapted to attain the ends and advantages mentioned as well as those that are inherent therein. The particular embodiments disclosed above are illustrative only, as the various embodiments may be modified and practiced in different but equivalent manners apparent to those skilled in the art having the benefit of the teachings herein. Furthermore, no limitations are intended to the details of construction or design herein shown, other than as described in the claims below. It is, therefore, evident that the particular illustrative embodiments disclosed above may be altered or modified and all such variations are considered within the scope and spirit of the present invention.

[0062] As used herein, the words "comprise," "have," "include," and all grammatical variations thereof are each intended to have an open, non-limiting meaning that does not exclude additional elements or steps. While compositions, systems, and methods are described in terms of "comprising," "containing," or "including" various components or steps, the compositions, systems, and methods also can "consist essentially of" or "consist of" the various components and steps. It should also be understood that, as used herein, "first," "second," and "third," are assigned arbitrarily and are merely intended to differentiate between two or more zones, sealing elements, *etc.*, as the case may be, and do not indicate any sequence. Furthermore, it is to be understood that the mere use of the word "first" does not require that there be any "second," and the mere use of the word "second" does not require that there be any "third," *etc.*

[0063] Whenever a numerical range with a lower limit and an upper limit is disclosed, any number and any included range falling within the range is specifically disclosed. In particular, every range of values (of the form, "from about a to about b," or, equivalently, "from approximately a to b," or, equivalently, "from approximately a - b") disclosed herein is to be understood to set forth every number and range encompassed within the broader range of values. Also, the terms in the claims have their plain, ordinary meaning unless otherwise explicitly and clearly defined by the patentee. Moreover, the indefinite articles "a" or "an," as used in the claims, are defined herein to mean one or more than one of the elements that it introduces. If there is any conflict in the usages of a word or term in this specification and one or more patent(s) or other documents that may be incorporated herein by reference, the definitions that are consistent with this specification should be adopted.

**What is claimed is:**

1. A well system comprising:  
a wellbore that penetrates a subterranean formation; and  
a downhole tool comprising a sealing element, wherein the sealing element comprises:  
an elastomer matrix; and  
a substance embedded within the elastomer matrix, wherein the substance expands at a phase change temperature.
2. The well system according to Claim 1, wherein the downhole tool is selected from a sleeve, a valve, a sensor, an actuator, a telemetry tool, a pressure balancing seal, a packer assembly, a plug, or a liner hanger.
3. The well system according to Claims 1 or 2, wherein the sealing element creates a seal between components of the downhole tool, and wherein the sealing element is an O-ring, gland seal, stack seal, or gasket.
4. The well system according to any one of the preceding claims, wherein the sealing element creates a seal between an outside of a mandrel of the downhole tool and the inside of a wall of the wellbore or the inside of a tubing string, and wherein the downhole tool is a packer assembly, a liner hanger, or a plug.
5. The well system according to any one of the preceding claims, wherein the elastomer of the elastomer matrix is a non-reactive polymer, a degradable polymer, or a polymer that swells in the presence of a fluid.
6. The well system according to any one of the preceding claims, wherein the substance expands with an increase in temperature at or above the phase change temperature.
7. The well system according to Claim 6, wherein the substance is an organic-based substance.

8. The well system according to Claim 7, wherein the organic-based substance is selected from the group consisting of: a polymeric plastic; a thermoplastic comprising acrylonitrile butadiene styrene, polypropylene, nylon 6/6, acetal, polycarbonate, or polyester; a semi-crystalline organic-based substance; or a wax comprising paraffin or stearic acid.
9. The well system according to Claim 7, wherein the sealing element further comprises a second organic-based substance, wherein the second organic-based substance has a different phase change temperature than the organic-based substance.
10. The well system according to Claim 7, wherein the organic-based substance is in the form of particles, and wherein the particles are encapsulated in a shell.
11. The well system according to any one of Claims 1 – 6, wherein the substance expands with a decrease in temperature at or below the phase change temperature.
12. The well system according to Claim 11, wherein the substance is a metal-based substance.
13. The well system according to Claim 12, wherein the metal-based substance comprises pure metals or metal alloys comprising bismuth, gallium, germanium, silicon, antimony, tin, lead, cadmium, indium, magnesium, manganese, zinc, thallium, mercury, lithium, sodium, potassium, and combinations thereof.
14. The well system according to Claim 12, wherein the sealing element further comprises a second metal-based substance, wherein the second metal-based substance has a different phase change temperature than the metal-based substance.
15. The well system according to any one of Claims 1 – 6 or 11, wherein the substance expands with an increase in temperature at or above the phase change temperature, and wherein the sealing element further comprises a second substance, wherein the second substance expands with a decrease in temperature at or below the phase change temperature.

16. The well system according to any one of Claims 1 – 6, 11, or 15, wherein the substance is selected such that the substance expands at least 1% in volume.
17. The well system according to any one of Claims 1 – 6, 11, 15, or 16, wherein the substance is in the form of particles having a particle size in the range of 10 millimeters to 1,000 nanometers.
18. The well system according to Claim 17, wherein the particles are interspersed throughout the elastomer matrix.

19. A method of creating a seal within a wellbore comprising:
- introducing a downhole tool into the wellbore, wherein the downhole tool comprises a sealing element, wherein the sealing element comprises:
    - an elastomer matrix; and
    - a substance embedded within the elastomer matrix, wherein the substance expands at a phase change temperature; and
  - causing or allowing the sealing element to create the seal within the wellbore.

20. A downhole tool comprising:
- a mandrel; and
  - a sealing element located adjacent to the mandrel, wherein the sealing element comprises:
    - an elastomer matrix; and
    - a substance embedded within the elastomer matrix, wherein the substance expands at a phase change temperature.