United States Patent Application Publication 20250257497
Kind Code A1
Publication Date August 14, 2025
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NANOBUBBLES FOR PREPARATION OF SPUN FIBROUS MATERIALS

Abstract

Provided herein are methods that involve the use of nanobubbles for preparing spun fibers. One such method includes (a) introducing a first dope fluid comprising a first polymer into a first opening of a spinneret; and (b) extruding a fiber jet comprising the first polymer from the spinneret, optionally into a coagulation bath comprising a fiber-forming coagulation medium, to form the fiber; wherein the first dope fluid, and optionally the coagulation bath, comprises nanobubbles.

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Family ID: **96660473**

Appl. No.: **19/046113**

Filed: **February 05, 2025**

Related U.S. Application Data

us-provisional-application US 63551631 20240209

Publication Classification

Int. Cl.: **D01D5/247** (20060101); **D01D5/00** (20060101); **D01D5/06** (20060101); **D01D5/24** (20060101); **D01D5/34** (20060101); **D01D10/02** (20060101)

U.S. Cl.:

CPC **D01D5/247** (20130101); **D01D5/0038** (20130101); **D01D5/06** (20130101); **D01D5/24** (20130101); **D01D5/34** (20130101); **D01D10/02** (20130101); D10B2401/10 (20130101)

Background/Summary

CLAIM OF PRIORITY [0001] This application claims priority to U.S. Provisional Application Ser. No. 63/551,631, filed on Feb. 9, 2024, the entire contents of which are hereby incorporated by reference.

TECHNICAL FIELD

[0002] This disclosure relates to preparation of spun fibrous materials.

BACKGROUND

[0003] Spun fibrous materials include a wide range of materials that are often made up of many small fibers that are bundled together. Spun fibrous materials can be used in a wide range of applications including filtration, fiber optics, water treatment, energy storage, biofuel production, gas separation, and biomedical applications.

SUMMARY

[0004] The inventors have discovered that including nanobubbles during spinning methods for producing spun fibrous materials can result in spun fibrous materials that exhibit increased porosity and improved surface roughness compared to conventionally prepared spun fibrous materials. Nanobubbles can be included in one or more components used in the spinning method, for example, in the dope fluid, the bore fluid, the coagulation medium, or combinations thereof. The present disclosure also encompasses use of nanobubble generators to generate nanobubbles for introduction into one or more of these components of the spinning methods.

[0005] Accordingly, aspects of the present disclosure provide a method of forming a fiber comprising (a) introducing a first dope fluid comprising a first polymer into a first opening of a spinneret; and (b) extruding a fiber jet comprising the first polymer from the spinneret into a coagulation bath comprising a fiber-forming coagulation medium to form a fiber, wherein the first dope fluid, the coagulation bath, or both comprise nanobubbles.

[0006] In some embodiments, the first dope fluid comprises a composition in which the first polymer is dissolved or dispersed in a solvent selected from the group consisting of aqueous solvents, organic solvents, and combinations thereof.

[0007] In some embodiments, methods described herein further comprise at least partially evaporating the solvent after extruding the fiber jet from the spinneret and before introducing the fiber jet into the coagulation bath.

[0008] In some embodiments, the first dope fluid comprises a flowable polymer.

[0009] In some embodiments, methods described herein further comprise introducing a second dope fluid comprising a second polymer into a second opening of the spinneret and extruding a fiber jet comprising the first polymer and the second polymer from the spinneret into the coagulation bath to form a composite fiber comprising a first layer comprising the first polymer and a second layer comprising the second polymer in which the first and second layers are in a coaxial arrangement, wherein the dope fluid, the second dope fluid, coagulation bath, or combination thereof comprise nanobubbles.

[0010] In some embodiments, methods described herein further comprise contacting the fiber with a second dope fluid comprising a second polymer to form a composite fiber comprising a first layer comprising the first polymer and a second layer comprising the second polymer in which the first and second layers are in a coaxial arrangement, wherein the first dope fluid, the second dope fluid, coagulation bath, or combination thereof comprise nanobubbles.

[0011] In some embodiments, methods described herein further comprise introducing a bore fluid comprising an aqueous solvent, organic solvent, or combination thereof into a second opening of the spinneret; extruding a fiber jet comprising the first polymer and the bore fluid from the spinneret; and removing the bore fluid to form a hollow fiber, wherein the first dope fluid, the bore

fluid, coagulation bath, or combination thereof comprise nanobubbles.
[0012] Aspects of the present disclosure provide a method of forming a fiber comprising (a) introducing a first dope fluid comprising a first polymer into a first opening of a spinneret; and (b) extruding a fiber jet comprising the first polymer from the spinneret to form a fiber, wherein the first dope fluid comprises nanobubbles.
[0013] In some embodiments, the first dope fluid comprises a composition in which the first polymer is dissolved or dispersed in a solvent selected from the group consisting of aqueous solvents, organic solvents, and combinations thereof.
[0014] In some embodiments, methods described herein further comprise removing the solvent by contacting the fiber jet with a heated roller. In some embodiments, methods described herein further comprise removing the solvent by introducing the fiber jet into a heated gas chamber.
[0015] In some embodiments, the first dope fluid comprises a flowable polymer.
[0016] In some embodiments, methods described herein further comprise introducing a second dope fluid comprising a second polymer into a second opening of the spinneret; and extruding a fiber jet comprising the first polymer and the second polymer from the spinneret to form a composite fiber comprising a first layer comprising the first polymer and a second layer comprising the second polymer in which the first and second layers are in a coaxial arrangement, wherein the first dope fluid, the second dope fluid, or combination thereof comprise nanobubbles.
[0017] In some embodiments, methods described herein further comprise contacting the fiber with a second dope fluid comprising a second polymer to form a composite fiber comprising a first layer comprising the first polymer and a second layer comprising the second polymer in which the first and second layers are in a coaxial arrangement, wherein the first dope fluid, the second dope fluid, or combination thereof comprise nanobubbles.
[0018] In some embodiments, methods described herein further comprise introducing a bore fluid comprising an aqueous solvent, organic solvent, or combination thereof into a second opening of the spinneret; extruding a fiber jet comprising the first polymer and the bore fluid from the spinneret, and removing the bore fluid to form a hollow fiber, wherein the first dope fluid, the bore fluid, or combination thereof comprise nanobubbles.
[0019] In some embodiments, methods described herein further comprise providing a collector for collecting fibers from the spinneret and creating an electrostatic field between the spinneret and collector by applying a high voltage to the spinneret while grounding the collector.
[0020] The approaches described here advantageously can be used to control porosity and pore size distribution of fibers. For instance, hollow fibers produced with the use of nanobubbles can have improved filtration capabilities because of their improved permeability as compared to fibers produced without nanobubbles. This enables use of less filtration material to provide a similar filtration effect. Such advantages are relevant, e.g., for IV cartridge filters. In some examples, fibers produced with the use of nanobubbles can have improved permeability without loss of retentate (also referred to as concentrate) rejection capabilities compared to fibers produced without nanobubbles.
[0021] Other features and advantages of the disclosure will be apparent from the following detailed description, and from the claims.

Description

BRIEF DESCRIPTION OF DRAWINGS
[0022] FIGS. **1**A and **1**B show schematic depictions of example wet-spinning methods involving use of nanobubbles (NB) for preparing spun fibers.
[0023] FIGS. **2**A and **2**B show schematic depictions of example dry-spinning methods involving use of nanobubbles (NB) for preparing spun fibers.

[0024] FIG. **3** shows a schematic depiction of an example of an electrospinning method involving use of nanobubbles (NB) for preparing spun fibers.
[0025] FIG. **4** shows a schematic depiction of an example of a thermally induced phase separation (TIPS) method involving use of nanobubbles (NB) for preparing spun fibers.
[0026] FIG. **5** shows a schematic depiction of an example of a melt spinning and cold-stretching (MSCS) method involving use of a nanobubble generator (NBG) for preparing spun fibers.

DETAILED DESCRIPTION

[0027] The methods described herein are directed to using nanobubbles for preparing spun fibrous materials including spun fibers (e.g., solid fibers, hollow fibers, and co-axial solid fibers). Generally, spun fibrous materials are prepared from polymer compositions including nanobubbles, among other components. Such polymer compositions include dope fluid, molten polymer, or both. For instance, the dope fluid comprises a composition in which the polymer is dissolved or dispersed in a nanobubble-containing solvent such as an aqueous solvent, an organic solvent, or combinations thereof. The nanobubble size and concentration in the polymer composition, such as a dope fluid, can be selected to tune the porosity and surface roughness of the resulting spun fibrous material. Alternatively, or in addition to, the porosity and surface roughness of the resulting spun fibrous material can be tuned by selection of the nanobubble size and concentration in the coagulation medium, the bore fluid, or both the coagulation medium and the bore fluid. Nanobubble size and concentration can also be selected to tune pore size distribution, which in turn can tune porosity and surface roughness. For example, pore size distribution can be difficult to control when forming fibers using electrospinning methods, and therefore nanobubble size and concentration can be selected to tune pore size distribution when forming fibers using electrospinning methods.
[0028] Forming fibers using spinning methods that include nanobubbles can produce fibers having improvements over conventionally formed fibers. For example, fibers formed using methods involving nanobubbles can have improved filtration capabilities resulting at least in part from increased porosity due to the formation of a large number of small pores.

Methods of Forming Fibers

[0029] Methods described herein encompass using nanobubbles in any fiber spinning method known in the art or described herein. Non-limiting examples of fiber spinning methods in which nanobubbles can be used include wet-spinning (e.g., bath coagulation, tube coagulation, or a combination thereof), dry-spinning (e.g., precipitation dry-spinning, hot-gas dry-spinning, or a combination thereof), electrospinning (e.g., solution electrospinning, melt electrospinning, or a combination thereof), thermally induced phase separation (TIPS), melt spinning and cold-stretching (MSCS), and combinations of any of these.
[0030] In some examples, methods described herein can include using nanobubbles in a wet-spinning method for forming fibers. Such methods involve extruding a fiber jet into a coagulation bath comprising fiber-forming coagulation medium.
[0031] As shown in FIG. **1**A, an example wet-spinning method **100** includes introducing a dope fluid **102** including a polymer and nanobubbles into an opening of a spinneret **104**. The dope fluid **102** can be a flowable polymer or a polymer dissolved or dispersed in a solvent. A bore fluid **106** including a solvent (e.g., an aqueous solvent, an organic solvent, or a combination thereof) and nanobubbles is introduced into another opening in the spinneret **104**. A fiber jet (also referred to as a fiber stream) **108** including the polymer and the bore fluid **106** from the spinneret **104** is extruded into a coagulation bath **110** including a fiber-forming coagulation medium **112** and nanobubbles. The coagulation bath can be a nonsolvent bath, where a nonsolvent induces precipitation for fiber formation, and Solvent Bath, where a solvent is used as the coagulating medium. The solvent concentration is adjusted based on fiber formation.
[0032] The bore fluid **106** is removed to form a hollow fiber **114**. For instance, the bore fluid **106** can be removed by invert phase separation, precipitation, evaporation, or other suitable methods.

[0033] In some examples, the dope fluid **106** can include a solvent (e.g., an aqueous solvent, an organic solvent, or a combination thereof) with the polymer dissolved or dispersed therein. After the fiber jet **108** is extruded from the spinneret **104** and before introducing the fiber jet **108** into the coagulation bath **110**, the solvent can be at least partially evaporated.
[0034] Although FIG. **1**A depicts a wet-spinning method in which nanobubbles are included in each of the dope fluid, the bore fluid, and the coagulation medium, wet-spinning methods described herein encompass use of nanobubbles in one or more of the dope fluid, the bore fluid, and the coagulation medium, e.g., only in the dope fluid; only in the bore fluid; only in the coagulation medium; in the dope fluid and the bore fluid but not in the coagulation medium; in the dope fluid and the coagulation medium but not in the bore fluid; in the bore fluid and the coagulation medium but not in the dope fluid; or in the dope fluid, the bore fluid, and the coagulation medium.
[0035] Although FIG. **1**A depicts a wet-spinning method in which bore fluid is used to form hollow fibers, the present disclosure encompasses wet-spinning methods that make use of only a dope fluid and without use of a bore fluid. These methods can be used to form solid fibers or co-axial fibers. For example, with reference to FIG. **1**A, such methods can comprise introducing the dope fluid **102** into the opening of the spinneret **104** and extruding a fiber jet **108** comprising the polymer of the dope fluid **102** from the spinneret **104** into the coagulation bath **110** to form the fiber. In such instances, the dope fluid, the coagulation bath, or both the dope fluid and the coagulation bath can comprise nanobubbles.
[0036] In some examples, the resulting fiber **114** is contacted with a second dope fluid including a second polymer to form a composite fiber. The composite fiber includes a first, internal layer of the polymer from the dope fluid **102** and a second, coaxial external layer of the second polymer from the second dope fluid. Nanobubbles can be included in the second dope fluid, in addition to or instead of any of the dope fluid **102**, the bore fluid, or the coagulation medium. In some examples, the second dope fluid is used without a bore fluid.
[0037] In some examples, multiple dope fluids can be used, e.g., with or without a bore fluid. The use of multiple dope fluids produces coaxial fibers. Generally, multiple tubes are used to produce coaxial fibers, with each dope fluid flowing through a corresponding tube. The polymer from the dope fluid that passes through an innermost tube forms the inner layer of the coaxial fiber, and the polymer from the dope fluid that passes through an outermost tube forms the outer layer of the coaxial fiber. The further use of a bore fluid produces hollow coaxial fibers.
[0038] Referring to FIG. **1**B, an example wet-spinning method **150** includes introducing a first dope fluid **152** including a first polymer into a first opening of a spinneret **154** and introducing a second dope fluid **155** including a second, different polymer into a second opening of the spinneret **154**. A fiber jet **158** including the first and second polymers is extruded from the spinneret **154** into a coagulation bath **160** including a fiber-forming coagulation medium **162**. The resulting fiber **164** is a composite fiber including the first and second polymers, having a first layer including the first polymer and a second layer coaxial with the first layer and including the second polymer.
[0039] In the example method of FIG. **1**B, nanobubbles can be present in the first dope fluid **152**, the second dope fluid **155**, or the coagulation medium **162**, or any combination thereof. When a bore fluid is also used, nanobubbles can be present in the bore fluid in addition to or instead of nanobubbles being present in the first or second dope fluid or the coagulation medium.
[0040] FIGS. **1**A and **1**B illustrate wet-spinning methods involving coagulation baths into which polymer is extruded for fiber formation. Nanobubbles can also be used in conjunction with wet-spinning methods involving tube coagulation, in which a spinneret is submerged in a coagulating bath contained in a tube, allowing fiber formation as the polymer travels through the tube surrounded by coagulation medium.
[0041] In some examples, methods described herein can include using nanobubbles in a dry-spinning methods for forming fibers. Such methods involve forming fibers by evaporating solvent in a fiber jet using a hot gas, a heated roller, or a combination thereof. Dry-spinning with hot gas

allows partial solvent evaporation before reaching a coagulation bath. Use of a heated roller promotes solvent evaporation as the polymer solution is extruded onto a heated roller.

[0042] Other approaches to dry-spinning are also within the scope of this disclosure, such as precipitation dry-spinning, which dissolves the polymer in a nonsolvent; and hot-gas dry-spinning, which extrudes the polymer solution into a chamber with hot gases, leading to solvent evaporation and fiber formation

[0043] As shown in FIG. **2**A, an example dry spinning method **200** can include introducing a dope fluid **202** including a polymer and nanobubbles into an opening of a spinneret **204**. The dope fluid **202** can be a flowable polymer or a polymer dissolved or dispersed in a solvent. A bore fluid **206** including a solvent and nanobubbles is introduced into another opening in the spinneret **204**. A fiber jet **208** comprising the polymer and the bore fluid **206** from the spinneret **204** is extruded to form a fiber **214**, such as a hollow fiber.

[0044] In some examples, the fiber jet **208** is extruded onto a heated roller **218** to remove solvent, e.g., to remove the solvent of the dope fluid **202** and/or to remove the bore fluid **206**. In some examples, the fiber jet **208** is exposed to heated air **216**, e.g., by introducing the fiber jet **208** into a heated gas chamber, to remove solvent, e.g., to remove the solvent of the dope fluid **202** and/or to remove the bore fluid **206**.

[0045] In some examples, the resulting fiber **214** is contacted with a second dope fluid including a second polymer to form a composite fiber. The composite fiber includes a first, internal layer of the polymer from the dope fluid **202** and a second, coaxial external layer of the second polymer from the second dope fluid. Nanobubbles can be included in the second dope fluid, in addition to or instead of any of the dope fluid **202**, the bore fluid, or the coagulation medium. In some examples, the second dope fluid is used without a bore fluid.

[0046] Although FIG. **2**A depicts a dry-spinning method in which nanobubbles are included in both the dope fluid and the bore fluid, dry-spinning methods described herein encompass use of nanobubbles in only the dope fluid, only the bore fluid, or both the dope fluid and the bore fluid.

[0047] Although FIG. **2**A depicts a dry-spinning method in which bore fluid is used to form hollow fibers, the present disclosure encompasses dry-spinning methods that make use of only a dope fluid and without use of a bore fluid. These methods can be used to form solid fibers or co-axial fibers. For example, such methods can comprise introducing a dope fluid comprising a polymer dissolved or dispersed in a solvent (e.g., an aqueous solvent, an organic solvent, or a combination thereof) into an opening of a spinneret, and extruding a fiber jet comprising the polymer and the solvent from the spinneret; and removing the solvent to form a fiber. In such instances, the dope fluid can comprise nanobubbles.

[0048] In some examples, multiple dope fluids can be used, e.g., with or without a bore fluid. Referring to FIG. **2**B, an example dry spinning method **250** includes introducing a first dope fluid **252** including a polymer into an opening of a spinneret **254** and introducing a second dope fluid **255** including a second, different polymer into a second opening of the spinneret **254**. A fiber jet **268** including the first and second polymers is extruded from the spinneret **254** to form a fiber **264**. The fiber **264** is a composite fiber including the first and second polymers, having a first layer including the first polymer and a second layer coaxial with the first layer and including the second polymer.

[0049] In the example process of FIG. **2**B, nanobubbles can be present in the first dope fluid **252**, the second dope fluid **255**, or both. When a bore fluid is also used, nanobubbles can be present in the bore fluid in addition to or instead of nanobubbles being present in the first or second dope fluid.

[0050] In some examples, dry-spinning and wet-spinning are used together for fiber formation. For instance, a polymer is dissolved in a solvent, spun into a dry air stream, and immersed in a coagulation bath. Nanobubbles can be included in dope and/or bore fluid and/or in the coagulation medium.

[0051] In some examples, methods described herein can include using nanobubbles in an electrospinning method for forming fibers. Such methods involve applying a high voltage to the spinneret and grounding the collector to create an electrostatic field between the spinneret and the collector.

[0052] As shown in FIG. **3**, an example electrospinning method **300** described herein can include introducing a dope fluid **302** including a polymer and nanobubbles into an opening of a spinneret **304** in which a high voltage is applied and introducing a bore fluid **306** including a solvent and nanobubbles into another opening in the spinneret **304**. The purpose of the high voltage is to overcome the surface tension of the polymer solution by charging the polymer molecules. The electrostatic field induces repulsion among like-charged polymer molecules, resulting in the ejection of a fine jet that moves towards a grounded collector **320** due to the influence of the electric field. A fiber jet **308** including the polymer is extruded from the spinneret **304** toward the grounded collector **320**. A fiber is formed as the fiber jet **308** travels from the spinneret **304** to the grounded collector **320**, where the fiber is collected.

[0053] Although FIG. **3** depicts an electrospinning method in which nanobubbles are included in both the dope fluid and the bore fluid, electrospinning methods described herein encompass use of nanobubbles in only the dope fluid, only the bore fluid, or both the dope fluid and the bore fluid.

[0054] Although FIG. **3** depicts an electrospinning method in which bore fluid is used to form hollow fibers, the present disclosure encompasses electrospinning methods that make use of only a dope fluid and without use of a bore fluid. These methods can be used to form solid fibers or co-axial fibers. For example, such methods can comprise introducing a dope fluid comprising a polymer into an opening of a spinneret; and extruding a fiber jet comprising the polymer from the spinneret into a grounded collector to form the fiber. In such instances, the dope fluid can comprise nanobubbles. Moreover, multiple dope fluids can be used to form coaxial fibers, e.g., as described above, and can be used with or without a bore fluid.

[0055] Various types of electrospinning are within the scope of this disclosure. For solution electrospinning (where polymer is dissolved in a solution), solvent evaporation occurs as the jet travels, leading to the formation of fine fibers. For melt electrospinning (where polymer melt is used directly and subjected to an electric field), fiber solidification as the jet travels towards collector while getting cooled by the surrounding air or gas. These fibers are collected on the grounded collector, resulting in the creation of a layer of interconnected fibers or a nonwoven mat.

[0056] In some examples, methods described herein can include using nanobubbles in a thermally induced phase separation (TIPS) method for forming fibers. Such methods involve extruding polymer and diluent from a screw extruder at a high temperature into a spinneret. Heat can be applied to improve the dispersion or solubility of polymer in the diluent., and then extruding a fiber jet into a coagulation bath comprising fiber-forming coagulation medium to induce phase separation. This technique can be done using both wet-spinning methods by using a coagulation bath and dry-spinning method, e.g., using various evaporation and precipitation phase separation techniques.

[0057] As shown in FIG. **4**, an example TIPS method **400** can include extruding polymer **424** and diluent **422** including nanobubbles from a screw extruder **426** at a high temperature into an opening in a spinneret **404** and introducing a bore fluid **406** including a solvent and nanobubbles into another opening in the spinneret **404**. A fiber jet **408** including the polymer **424** and the bore fluid **406** is extruded from the spinneret **404** into a coagulation bath **410** comprising a fiber-forming coagulation medium **412** and nanobubbles. The bore fluid **406** is removed to form a hollow fiber **414**.

[0058] Although FIG. **4** depicts a TIPS method in which nanobubbles are included in each of the diluent, the bore fluid, and the coagulation medium, TIPS methods described herein encompass use of nanobubbles in one or more of the diluent, the bore fluid, and the coagulation medium, e.g., only in the diluent; only in the bore fluid; only in the coagulation medium; in the diluent and the bore fluid but not in the coagulation medium; in the diluent and the coagulation medium but not in the bore fluid; in the bore fluid and the coagulation medium but not in the diluent; or in the diluent, the bore fluid, and the coagulation medium.

[0059] Although FIG. **4** depicts a TIPS method in which bore fluid is used to form hollow fibers, the present disclosure encompasses encompass TIPS methods that make use of only a diluent and without use of a bore fluid. These methods can be used to form solid fibers or co-axial fibers. For example, such methods can comprise extruding polymer and diluent comprising nanobubbles from a screw extruder at a high temperature into an opening in a spinneret; and extruding a fiber jet comprising the polymer from the spinneret into a coagulation bath comprising a fiber-forming coagulation medium to form the fiber. In such instances, the diluent, the coagulation bath, or both the diluent and the coagulation bath can comprise nanobubbles.

[0060] In one example, methods described herein can include using nanobubbles in a melt spinning and cold-stretching (MSCS) method for forming fibers. Such methods involve heating a polymer such that it melts; extruding a fiber jet comprising the polymer; quenching the fiber jet with air to form a fiber; and cold-stretching the formed fiber to induce pore formation.

[0061] As shown in FIG. **5**, an example MSCS method **500** described herein can include extruding a polymer **524** from a screw extruder **526** at a high temperature to form a polymer melt **528** that is flowed through a nanobubble generator **530** to introduce nanobubbles into the polymer melt, which is introduced into an opening in a spinneret **504**. Nitrogen gas **532** is also flowed into the spinneret **504**. A fiber jet **508** including the polymer is air quenched **532** to form a hollow fiber **514**. After the hollow fiber **514** is formed, cold-stretching of the hollow fiber **514** is performed to induce pore formation.

[0062] Although FIG. **5** depicts a MSCS method in which nitrogen gas is used to form hollow fibers, the present disclosure encompasses MSCS methods that lack use of nitrogen gas, which are used to form solid fibers or co-axial fibers. For example, such methods can comprise extruding a polymer from a screw extruder at a high temperature to form a polymer melt; flowing the polymer melt through a nanobubble generator to introduce nanobubbles into the polymer melt; introducing the polymer melt comprising nanobubbles into an opening in a spinneret; extruding a fiber jet comprising the polymer; quenching the fiber jet with air to form a solid fiber; and cold-stretching the solid fiber to induce pore formation.

[0063] Any of the methods of forming fibers described herein can include one or more dope fluids, e.g., 1, 2, 3, 4, or more dope fluids. In such instances, one or more of the dope fluids can comprise nanobubbles.

[0064] When methods involve two or more dope fluids, one dope fluid can be introduced into a spinneret and one or more additional dope fluids can be introduced into one or more additional openings in the spinneret. Alternatively, or in addition to, the one or more additional dope fluids can be contacted with a fiber.

[0065] For example, methods described herein can comprise introducing a first dope fluid comprising a first polymer into a first opening of a spinneret; introducing a second dope fluid comprising a second polymer into a second opening of the spinneret; and extruding a fiber jet comprising the first polymer and the second polymer from the spinneret into a coagulation bath to form a composite fiber comprising a first layer comprising the first polymer and a second layer comprising the second polymer in which the first and second layers are in a coaxial arrangement. In such instances, nanobubbles can be included in the first dope fluid, the second dope fluid, the coagulation bath, or a combination of any of these.

[0066] In another example, methods described herein can comprise introducing a first dope fluid comprising a first polymer into a first opening of a spinneret; extruding a fiber jet comprising the first polymer from the spinneret into a coagulation bath to form the fiber; and contacting the fiber with a second dope fluid comprising a second polymer to form a composite fiber comprising a first layer comprising the first polymer and a second layer comprising the second polymer in which the first and second layers are in a coaxial arrangement. In such instances, nanobubbles can be included in the first dope fluid, the second dope fluid, the coagulation bath, or a combination of any of these.

[0067] Any of the methods of forming fibers described herein can include use of a dope fluid comprising a flowable polymer or a composition in which a polymer is dissolved or dispersed in a solvent (e.g., an aqueous solvent, an organic solvent, or a combination thereof). In such instances, methods described herein can comprise at least partially evaporating the solvent after extruding the fiber jet from the spinneret and before introducing the fiber jet into the coagulation bath. The dope fluid can include nanobubbles or the dope fluid can be free of nanobubbles.

[0068] Any of the methods of forming fibers described herein can include use of a bore fluid to form a hollow fiber. In such instances, methods described herein can comprise introducing a dope fluid comprising a polymer into an opening of a spinneret; introducing a bore fluid into another opening of a spinneret; extruding a fiber jet comprising the polymer and the bore fluid from the spinneret into a coagulation bath; and removing the bore fluid to form a hollow fiber. In such instances, nanobubbles can be included in the bore fluid, the dope fluid, the coagulation bath, or a combination of any of these.

[0069] Any of the methods of forming fibers described herein can include removing a solvent by one or more evaporation processes, e.g., using a heated roller, a heated gas chamber, or a combination thereof.

[0070] Methods of forming fibers described herein can include coating any number of layers onto a fiber, e.g., coating an internal fiber with any number of layers. For example, methods described herein can include coating 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 or more layers onto an internal fiber.

Components for Use in Methods for Forming Fibers

[0071] Methods for forming fibers described herein can involve use of nanobubbles in a dope fluid, a bore fluid, a polymer, a diluent, a fiber-forming coagulation medium, or a combination of any of these

[0072] Dope fluids for use in methods described herein can include any solvent suitable for preparing fibers using a wet-spinning method. Non-limiting examples of solvents include acetone, dimethylformamide (DMF), dimethylacetamide (DMAc), sodium thiocyanate, sulfuric acid, zinc chloride, N-methylmorpholine N-oxide (NMMO), sodium hydroxide, dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), methanol, ethanol, formic acid, acetic acid, lithium chloride/dimethylacetamide (LiCl/DMAc), hexafluoroisopropanol (HFIP), ionic liquids, phosphoric acid, chlorinated solvents (e.g., methylene chloride), and combinations of any of these.

[0073] Dope fluids for use in methods described herein can include any solvent suitable for preparing fibers using a dry-spinning method. Non-limiting examples of solvents include acetone, dimethylformamide (DMF); dimethylacetamide (DMAc); dimethyl sulfoxide (DMSO); methylene chloride; tetrahydrofuran (THF); trichloroethylene; carbon disulfide; formic acid; chlorinated benzenes; hexafluoroisopropanol (HFIP); sulfuric acid; N,N-dimethylimidazole (DMI); hexamethylphosphoramide (HMPA); cyclohexanone; toluene; chloroform; dichloroethane; ethylene glycol; dichlorobenzene; methanol; 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP); propylene carbonate; isophorone; and combinations of any of these.

[0074] Bore fluids for use in methods described herein can include any solvent suitable for preparing fibers using a wet-spinning method or a dry-spinning method. Non-limiting examples of solvents include water, sulfuric acid, sodium sulfate/sodium chloride solutions, aqueous zinc chloride, calcium chloride solutions, aqueous ammonium sulfate, methanol, isopropanol, acetic acid, and combinations of any of these.

[0075] Polymers for use in methods described herein can include any polymer suitable for forming a fiber. Non-limiting examples of polymers include polyacrylonitrile, aramids, acrylic, cellulose, polyurethane, fluoropolymers, polyethylene, polyvinyl alcohol polymers, hydrophilic polymers, polyvinyl chloride polymers, and combinations thereof.

[0076] Diluents for use in methods described herein can include any diluent suitable for preparing fibers using a TIPS methods. Non-limiting examples of diluents include paraffin oil, dibutyl phthalate (DBP), glycerol, mineral oil, phthalates, polyethylene glycol (PEG), silicone oil, naphthalene, camphor, decahydronaphthalene, dioctyl phthalate (DOP), tetradecane, dodecane, cyclohexane, linseed oil, isopropyl myristate, limonene, octadecanol, castor oil, and combinations of any of these.
[0077] Fiber-forming coagulation medium for use in methods described herein can include any solvent suitable for preparing fibers using a wet-spinning method. Non-limiting examples of solvents include water, sulfuric acid, sodium sulfate, sodium hydroxide, zinc sulfate, calcium chloride, ammonium sulfate, methanol, ethanol, isopropanol, sodium chloride, acetic acid, copper sulfate, and combinations of any of these.
[0078] Any solvent suitable for preparing fibers using an electrospinning method can be used in methods described herein. Non-limiting examples of solvents include acetic acid, acetone, chloroform, dimethylformamide (DMF), dimethyl sulfoxide (DMSO), ethanol, hexafluoroisopropanol (HFIP), N,N-dimethylacetamide (DMAc), tetrahydrofuran (THF), toluene, water, and combinations of any of these.
Nanobubbles and Nanobubble Generators
[0079] Methods described herein encompass generating nanobubbles during a fiber spinning method. As used herein, the term “nanobubble” refers to a bubble that has a diameter of less than one micron. A microbubble, which is larger than a nanobubble, is a bubble that has a diameter greater than or equal to one micron and smaller than 50 microns. A macrobubble is a bubble that has a diameter greater than or equal to 50 microns. As used herein, a “nanobubble generator” refers to a device for generating nanobubbles.
[0080] Any method or apparatus known in the art or described herein can be used to generate nanobubbles in methods for forming fibers provided herein. Non-limiting examples of methods and apparatuses for generating nanobubbles that can be used in methods for forming fibers described herein are provided in U.S. Pat. Nos. 10,591,231 and 11,331,633, the entire contents of which are herein incorporated by reference for the purposes and subject matter referenced herein.
[0081] A nanobubble generator for use in methods for forming fibers described herein is capable of generating a high concentration of nanobubbles in fiber spinning methods, e.g., in the dope fluid, the bore fluid, the coagulation medium, the diluent, or any combination of these. In some embodiments, the nanobubble generator can generate nanobubbles at a concentration of at least 10.sup.6 nanobubbles per cm.sup.3. In some embodiments, the nanobubble concentration is at least 10.sup.7 nanobubbles per cm.sup.3, at least 10.sup.8 nanobubbles per cm.sup.3, at least 10.sup.9 nanobubbles per cm.sup.3, at least 10.sup.10 nanobubbles per cm.sup.3, or at least 10.sup.11 nanobubbles per cm.sup.3.
[0082] The nanobubble concentration is expressed as nanobubbles per cm.sup.3. It is measured by collecting 3 samples from the nanobubble generator and analyzing each sample within 20 minutes after it has been obtained by Nanoparticle Tracking Analysis using a Nanosight NS3000 analyzer available from Malvern PANalytical.
[0083] Any gas can be used to generate nanobubbles in methods for forming fibers described herein. Non-limiting examples of gases that can be used to generate nanobubbles include air, hydrogen, biogas, methane, carbon dioxide, nitrogen, oxygen, or ozone.
Uses and Applications
[0084] The fibers formed according to methods described herein can be suitable for a variety of uses and applications including uses and applications known in the art or described herein.
[0085] For example, solid fibers formed as described herein can be suitable for a variety of uses and applications including, but not limited to, filtration (e.g., water purification systems, air filters, medical filters such as those used for removing particulates from gases and liquids); textiles (e.g., production of non-woven fabrics for clothing, upholstery and home textiles, industrial textiles for

geotextiles and agriculture); medical uses (e.g., wound dressing, sutures and medical implants, drug delivery systems); reinforcement of materials (e.g., reinforcement in composite materials, concrete, construction materials, or any combination of these); insulation (e.g., thermal insulation in buildings and clothing, acoustic insulation in construction and automotive materials); consumer products (e.g., filters in vacuum cleaners and air purifiers, cosmetic applicators); packaging (e.g., cushioning material, protective packaging wraps); and energy (e.g., battery separators, fuel cell components, electrolyzer components).

[0086] In another example, hollow fibers formed as described herein can be suitable for a variety of uses and applications including, but not limited to, filtration (e.g., ultrafiltration, nanofiltration, and reverse osmosis membranes for water treatment, blood filters in medical dialyzers, gas separation membranes for CO**2** capture and oxygen enrichment); fiber optics (e.g., data transmission in telecommunications, medical endoscopy devices); textiles (e.g., high-performance sportswear for insulation); biotechnology (e.g., bioreactors for cell and enzyme immobilization; artificial organs and tissue engineering scaffolds); medical use (e.g., vascular grafts, catheters, cannulas); aerospace and automotive (e.g., lightweight materials for insulation and component reinforcement); and energy (e.g., battery separators, fuel cell components, electrolyzer components).

Other Embodiments

[0087] It is to be understood that while the document has been described in conjunction with the detailed description thereof, the foregoing description is intended to illustrate and not limit the scope of the document. Other aspects, advantages, and modifications are within the scope of the following claims.

Claims

1. A method of forming a fiber comprising: (a) introducing a first dope fluid comprising a first polymer into a first opening of a spinneret; and (b) extruding a fiber jet comprising the first polymer from the spinneret into a coagulation bath comprising a fiber-forming coagulation medium to form a fiber, wherein the first dope fluid, the coagulation bath, or both comprise nanobubbles.

2. The method of claim 1, wherein the first dope fluid comprises a composition in which the first polymer is dissolved or dispersed in a solvent selected from the group consisting of aqueous solvents, organic solvents, and combinations thereof.

3. The method of claim 2, further comprising at least partially evaporating the solvent after extruding the fiber jet from the spinneret and before introducing the fiber jet into the coagulation bath.

4. The method of claim 1, wherein the first dope fluid comprises a flowable polymer.

5. The method of claim 1, further comprising introducing a second dope fluid comprising a second polymer into a second opening of the spinneret and extruding a fiber jet comprising the first polymer and the second polymer from the spinneret into the coagulation bath to form a composite fiber comprising a first layer comprising the first polymer and a second layer comprising the second polymer in which the first and second layers are in a coaxial arrangement, wherein the dope fluid, the second dope fluid, coagulation bath, or combination thereof comprise nanobubbles.

6. The method of claim 1, further comprising contacting the fiber with a second dope fluid comprising a second polymer to form a composite fiber comprising a first layer comprising the first polymer and a second layer comprising the second polymer in which the first and second layers are in a coaxial arrangement, wherein the first dope fluid, the second dope fluid, coagulation bath, or combination thereof comprise nanobubbles.

7. The method of claim 1, further comprising introducing a bore fluid comprising an aqueous solvent, organic solvent, or combination thereof into a second opening of the spinneret; extruding a fiber jet comprising the first polymer and the bore fluid from the spinneret; and removing the bore fluid to form a hollow fiber, wherein the first dope fluid, the bore fluid, coagulation bath, or combination thereof comprise nanobubbles.

8. A method of forming a fiber comprising: (a) introducing a first dope fluid comprising a first polymer into a first opening of a spinneret; and (b) extruding a fiber jet comprising the first polymer from the spinneret to form a fiber, wherein the first dope fluid comprises nanobubbles.

9. The method of claim 8, wherein the first dope fluid comprises a composition in which the first polymer is dissolved or dispersed in a solvent selected from the group consisting of aqueous solvents, organic solvents, and combinations thereof.

10. The method of claim 9, further comprising removing the solvent by contacting the fiber jet with a heated roller.

11. The method of claim 9, further comprising removing the solvent by introducing the fiber jet into a heated gas chamber.

12. The method of claim 8, wherein the first dope fluid comprises a flowable polymer.

13. The method of claim 8, further comprising introducing a second dope fluid comprising a second polymer into a second opening of the spinneret; and extruding a fiber jet comprising the first polymer and the second polymer from the spinneret to form a composite fiber comprising a first layer comprising the first polymer and a second layer comprising the second polymer in which the first and second layers are in a coaxial arrangement, wherein the first dope fluid, the second dope fluid, or combination thereof comprise nanobubbles.

14. The method of claim 8, further comprising contacting the fiber with a second dope fluid comprising a second polymer to form a composite fiber comprising a first layer comprising the first polymer and a second layer comprising the second polymer in which the first and second layers are in a coaxial arrangement, wherein the first dope fluid, the second dope fluid, or combination thereof comprise nanobubbles.

15. The method of claim 8, further comprising introducing a bore fluid comprising an aqueous solvent, organic solvent, or combination thereof into a second opening of the spinneret; extruding a fiber jet comprising the first polymer and the bore fluid from the spinneret, and removing the bore fluid to form a hollow fiber, wherein the first dope fluid, the bore fluid, or combination thereof comprise nanobubbles.

16. The method of claim 9, further comprising providing a collector for collecting fibers from the spinneret and creating an electrostatic field between the spinneret and collector by applying a high voltage to the spinneret while grounding the collector.