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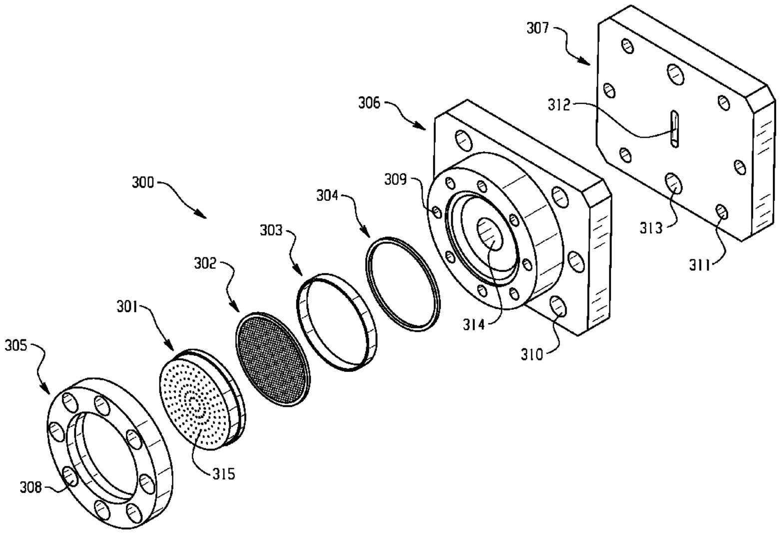
[Continued on next page]

(54) Title: METHOD OF PRODUCING FINE AMORPHOUS POLYMER FIBRES, FINE AMORPHOUS POLYMER|FIBRES, AND SPINNERET FOR PRODUCING SUCH FIBRES



(57) Abstract: A method, including extruding a melt including an amorphous polymer composition through a spinneret under a pressure from 400 to 1500 psi to produce a spun fiber; collecting the spun fiber on a feeding roll without drawing the spun fiber; producing a solidified fiber from the spun fiber. The solidified fiber can have a dpf of from greater than 0 to 2.5 dpf, and a shrinkage less than or equal to 2%. The method can also include collecting the solidified fiber onto a spool without subjecting the solidified fiber to a drawing step. A spinneret for producing fibers of at most 2.5 dpf from a composition comprising an amorphous polyetherimide, the spinneret comprising a die having a plurality of round melt channels but no distribution plates. Fibers produced by the method and from the spinneret are also disclosed.

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METHOD OF PRODUCING FINE AMORPHOUS POLYMER FIBRES, FINE AMORPHOUS POLYMER FIBRES, AND SPINNERET FOR PRODUCING SUCH FIBRES

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention relates generally to fibers and to systems, methods, and apparatus for producing fibers. More specifically, the invention relates to fine denier amorphous polymer fibers, such as fine denier polyetherimide fibers, and to systems, methods, and apparatus for producing such fibers by melt spinning the polymer without drawing the spun fibers.

2. Description of the related art

Synthetic fibers have been produced for many years with very established processes and process equipment that has been optimized for the melt and physical properties of semicrystalline materials, namely low melt viscosity, excellent heat stability, and crystallization. Traditionally synthetic fibers have been produced using semicrystalline materials which have a very low viscosity in a melt state, and require process or die design methods to produce an even melt distribution across the spinneret hole pattern. The spinnerets are designed to facilitate that even distribution of the melt. But these designs are not favorable to use with amorphous polymers, including thermoplastics such as polyetherimides. Processing amorphous thermoplastics into fibers using the melt spinning process is a new process being attempted on traditional melt spinning lines with limited success. Some of these issues can be attributed to the design of the processing equipment not being suitable for amorphous materials. Despite the need, there are no melt spinning lines or spinnerets that are specifically designed for producing amorphous thermoplastics into fine fibers by melt-spinning them without drawing the resultant fibers to reduce their denier.

Traditionally synthetic fibers have been produced using semicrystalline materials which crystallize upon drawing from the spinneret and are easily melt spun down to fine denier fibers of 2 denier per filament (dpf) and below. Amorphous materials do not form crystals upon drawing and therefore do not have enough elongation and strength during the drawing part of the process to be pulled down to 2 dpf and below using conventional melt spinning methods. Traditional process protocols are not suitable to convert certain amorphous engineering thermoplastic compositions, such as polyetherimide (PEI) pellets, into fine denier fibers, because the traditional processes result in limitations as to how fine a fiber can be achieved. A need exists for polyetherimide fibers having a dpf of 2 or lower. A method and processing techniques need to be developed that will allow the production of 2 dpf, and lower, fibers from amorphous engineering thermoplastics like PEI. Current attempts at producing fine denier fibers are made with conventional methods, and are either drawn in a post conversion process stretching operation, or not drawn down to 2 dpf and lower.

BRIEF SUMMARY OF THE INVENTION

An embodiment relates to a method including the steps of extruding a polymer melt through a spinneret under a pressure from 400 to 1500 psi to produce a spun fiber, collecting the spun fiber on a fowarding roll, sometimes also called a feeding roll, producing a solidified fiber from the spun fiber, and collecting the solidified fiber onto a spool without subjecting the solidified fiber to a drawing step. The melt can include an amorphous polymer composition, such as a polyetherimide. The solidified fiber can have a dpf within a range from greater than 0 up to 2.5 dpf, and a shrinkage of less than or equal to 2%.

Another embodiment relates to an undrawn amorphous polymer fiber having a denier less than 2.5 and a shrinkage from greater than 0 to less than or equal to 2%.

Still other embodiments relate to a spinneret for producing an amorphous undrawn polyetherimide fiber of at most 2.5 dpf from a composition including an amorphous polyetherimide, such as a polyetherimide. The spinneret can avoid the use of distribution plates and can operate at a pressure that is at least 40% less than the operating pressure of a spinneret comprising distribution plates. The spinneret can include a screen pack filter coupled to a die to distribute the composition to the die. The die can have a plurality of round melt channels, wherein each round melt channel has a length and a diameter, and wherein the ratio of length:diameter of each round melt channel is from 2:1 to 6:1.

BRIEF DESCRIPTION OF THE DRAWINGS

These and other features, aspects, and advantages will become better understood with reference to the following description and appended claims, and accompanying drawings where:

FIG. 1 is a schematic diagram of a prior art spinneret design containing two distribution plates that are absent in the design of various embodiments of the invention;

FIG. 2 is a schematic diagram of a 72 hole spinneret design having a center core distribution feeding three concentric rings of capillaries, according to various embodiments of the invention;

FIG. 3 is a schematic diagram of a 144 hole spinneret design having a screen pack filter for distribution feeding six concentric rings of capillaries, according to various embodiments of the invention; and

FIG. 4 is a schematic diagram of a prior art fiber production process that can be modified to employ the spinnerets according to various embodiments of the invention.

It should be understood that the various embodiments are not limited to the arrangements and instrumentality shown in the drawings.

DETAILED DESCRIPTION OF THE INVENTION

In the following detailed description and in the claims which follow, reference will be made to a number of terms which shall be defined to have the following meanings:

“Denier” is a unit of measure for the linear mass density of fibers. In this application and claims, it is defined as the mass in grams per 9,000 meters.

As use in this application and claims, a “spinneret” is a multi-pored device through which a plastic polymer melt is extruded to form fibers.

All numeric values are herein assumed to be modified by the term “about,” whether or not explicitly indicated. The term “about” generally refers to a range of numbers that one of skill in the art would consider equivalent to the recited value (i.e., having the same function or result). In many instances, the term “about” may include numbers that are rounded to the nearest significant figure.

An embodiment of the invention relates to a process for producing fine denier fibers from engineering thermoplastics such as polyetherimide.

In traditional processing of forming fibers by melt extrusion, high pressure (1000 to 2000 psi) is critical to maintain an even distribution of melt across the spinneret holes and where a quench apparatus is employed to control the cooling rate and thus the degree of crystallinity of the material as it is drawn out of the spinneret. Various embodiments of the invention avoid these conditions, which are not desirable for processing amorphous engineering thermoplastics into fine denier fibers. According to embodiments of the invention, the pressures can be lowered

(400 to 2000 psi) to reduce shear on the material in a melt state, and therefore decrease the negative effect of that abuse, namely drops or breaks in the fiber strands. It has been discovered that the higher viscosities of the amorphous thermoplastics in the melt state are capable of providing enough back pressure in the system to distribute the melt evenly across the spinneret. Upon exiting the spinneret, the material is not cooled in the quench cabinet, and actually, unexpectedly benefits from using heat in this space to slow the cooling rate of the amorphous materials, and reduce the quenching effect on the spun material. Using the methods described above, methods according to the present invention can successfully be used to melt spin polyetherimide fibers to 2 dpf and lower.

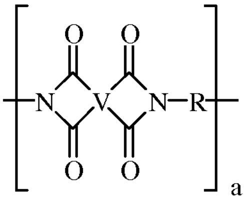
An embodiment relates to a method comprising a series of steps. The steps can be sequential or nonsequential. The method can include a step of extruding a melt through a spinneret to produce a spun fiber.

The melt can be extruded through the spinneret under a pressure within a range having a lower limit and/or an upper limit. The range can include or exclude the lower limit and/or the upper limit. The lower limit and/or upper limit can be selected from 100, 150, 200, 250, 300, 350, 400, 450, 500, 550, 600, 650, 700, 750, 800, 850, 900, 950, 1000, 1050, 1100, 1150, 1200, 1250, 1300, 1350, 1400, 1450, 1500, 1550, 1600, 1650, 1700, 1750, 1800, 1850, 1900, 1950 and 2000 psi. For example, according to certain preferred embodiments, the melt can be extruded through the spinneret under a pressure from 400 to 1500 psi.

The melt can comprise an amorphous polymer composition. The amorphous polymer composition can have a melt flow rate within a range having a lower limit and/or an upper limit. The range can include or exclude the lower limit and/or the upper limit. The lower limit and/or upper limit can be selected from any one of 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59 and 60 g/10 min. For example, according to certain preferred embodiments, the amorphous polymer composition can have a melt flow rate from 4 to 18 gram per 10 minutes (g/10 min).

The melt can comprise one or more crystalline materials. The amorphous polymer composition can comprise a polyimide. Polyimides include polyetherimides and polyetherimides copolymers. The polyetherimide can be selected from (i) polyetherimide homopolymers, e.g., polyetherimides, (ii) polyetherimide co-polymers, e.g., polyetherimide sulfones, and (iii) combinations thereof. Polyetherimides are known polymers and are sold by SABIC Innovative Plastics under the ULTEM®*, EXTEM®*, and SILTEM* brands (Trademark of SABIC Innovative Plastics IP B.V.).

In an embodiment, the polyetherimides are of formula (1):

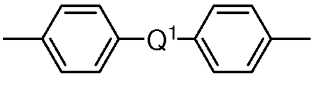


(1),

wherein a is more than 1, for example 10 to 1,000 or more, or more specifically 10 to 500.

The group V in formula (1) is a tetravalent linker containing an ether group (a "polyetherimide" as used herein) or a combination of an ether groups and arylene sulfone groups (a "polyetherimide sulfone"). Such linkers include but are not limited to: (a) substituted or unsubstituted, saturated, unsaturated or aromatic monocyclic and polycyclic groups having 5 to 50 carbon atoms, optionally substituted with ether groups, arylene sulfone groups, or a combination of ether groups and arylene sulfone groups; and (b) substituted or unsubstituted, linear or branched, saturated or unsaturated alkyl groups having 1 to 30 carbon atoms and optionally substituted with ether groups or a combination of ether groups, arylene sulfone groups, and arylene sulfone groups; or combinations comprising at least one of the foregoing. Suitable additional substitutions include, but are not limited to, ethers, amides, esters, and combinations comprising at least one of the foregoing.

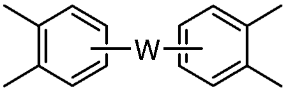
The R group in formula (1) includes but is not limited to substituted or unsubstituted divalent organic groups such as: (a) aromatic hydrocarbon groups having 6 to 20 carbon atoms and halogenated derivatives thereof; (b) straight or branched chain alkylene groups having 2 to 20 carbon atoms; (c) cycloalkylene groups having 3 to 20 carbon atoms, or (d) divalent groups of formula (2):



(2),

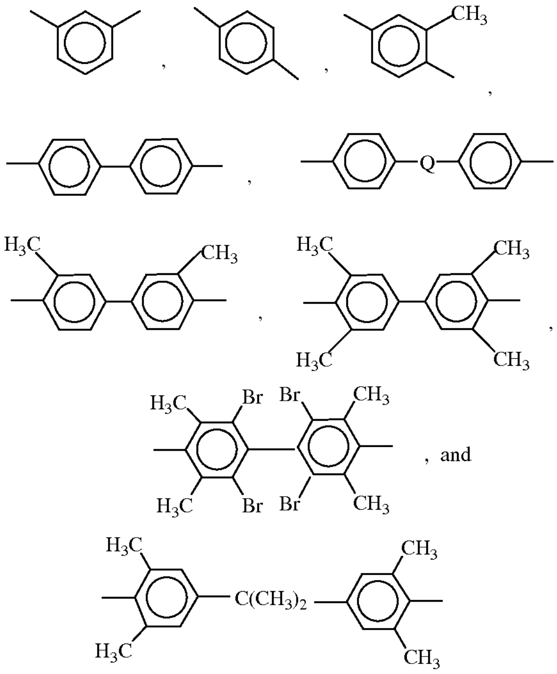
wherein Q^1 includes but is not limited to a divalent moiety such as -O-, -S-, -C(O)-, $-SO_2-$, -SO-, $-C_yH_{2y}-$ (y being an integer from 1 to 5), and halogenated derivatives thereof, including perfluoroalkylene groups.

In an embodiment, linkers V include but are not limited to tetravalent aromatic groups of formula (3):



(3),

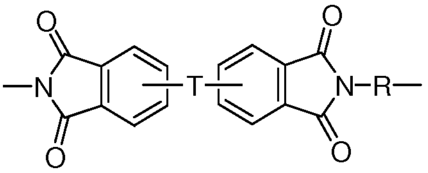
wherein W is a divalent moiety including -O-, $-SO_2-$, or a group of the formula -O-Z-O- wherein the divalent bonds of the -O- or the -O-Z-O- group are in the 3,3', 3,4', 4,3', or the 4,4' positions, and wherein Z includes, but is not limited, to divalent groups of formulas (4):



(4),

wherein Q includes, but is not limited to a divalent moiety including -O-, -S-, -C(O), $-SO_2-$, -SO-, $-C_yH_{2y}-$ (y being an integer from 1 to 5), and halogenated derivatives thereof, including perfluoroalkylene groups.

In a specific embodiment, the polyetherimide comprise more than 1, specifically 10 to 1,000, or more specifically, 10 to 500 structural units, of formula (5):

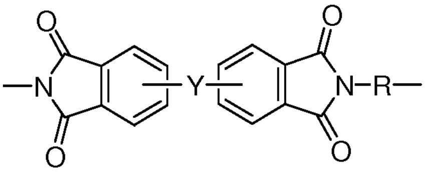


(5),

wherein T is -O- or a group of the formula -O-Z-O- wherein the divalent bonds of the -O- or the -O-Z-O- group are in the 3,3', 3,4', 4,3', or the 4,4' positions; Z is a divalent group of formula (3) as defined above; and R is a divalent group of formula (2) as defined above.

In another specific embodiment, the polyetherimide sulfones are polyetherimides comprising ether groups and sulfone groups wherein at least 50 mole % of the linkers V and the groups R in formula (1) comprise a divalent arylene sulfone group. For example, all linkers V, but no groups R, can contain an arylene sulfone group; or all groups R but no linkers V can contain an arylene sulfone group; or an arylene sulfone can be present in some fraction of the linkers V and R groups, provided that the total mole fraction of V and R groups containing an aryl sulfone group is greater than or equal to 50 mole%.

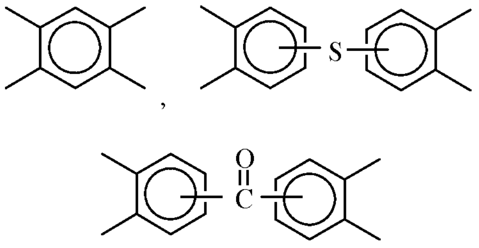
Even more specifically, polyetherimide sulfones can comprise more than 1, specifically 10 to 1,000, or more specifically, 10 to 500 structural units of formula (6):



(6),

wherein Y is -O-, -SO_2-, or a group of the formula -O-Z-O- wherein the divalent bonds of the -O-, SO_2-, or the -O-Z-O- group are in the 3,3', 3,4', 4,3', or the 4,4' positions, wherein Z is a divalent group of formula (3) as defined above and R is a divalent group of formula (2) as defined above, provided that greater than 50 mole% of the sum of moles Y + moles R in formula (2) contain -SO_2- groups.

It is to be understood that the polyetherimides and polyetherimide sulfones can optionally comprise linkers V that do not contain ether or ether and sulfone groups, for example linkers of formula (7):



, and

(7).

Imide units containing such linkers are generally be present in amounts ranging from 0 to 10 mole % of the total number of units, specifically 0 to 5 mole %. In an embodiment no additional linkers V are present in the polyetherimides and polyetherimide sulfones.

In another specific embodiment, the polyetherimide comprises 10 to 500 structural units of formula (5) and the polyetherimide sulfone contains 10 to 500 structural units of formula (6).

Polyetherimides and polyetherimide sulfones can be prepared by any suitable process. In an embodiment, polyetherimides and polyetherimide copolymers include polycondensation polymerization processes and halo-displacement polymerization processes.

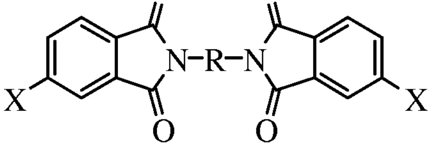
Polycondensation methods can include a method for the preparation of polyetherimides having structure (1) is referred to as the nitro-displacement process (X is nitro in formula (8)). In one example of the nitro-displacement process, N-methyl phthalimide is nitrated with 99% nitric acid to yield a mixture of N-methyl-4-nitrophthalimide (4-NPI) and N-methyl-3-nitrophthalimide (3-NPI). After purification, the mixture, containing approximately 95 parts of 4-NPI and 5 parts of 3-NPI, is reacted in toluene with the disodium salt of bisphenol-A (BPA) in the presence of a phase transfer catalyst. This reaction yields BPA-bisimide and $NaNO_2$ in what is known as the nitro-displacement step. After purification, the BPA-bisimide is reacted with phthalic anhydride in an imide exchange reaction to afford BPA-dianhydride (BPADA), which in turn is reacted with a diamine such as meta-phenylene diamine (MPD) in ortho-dichlorobenzene in an imidization-polymerization step to afford the product polyetherimide.

Other diamines are also possible. Examples of suitable diamines include: m-phenylenediamine; p-phenylenediamine; 2,4-diaminotoluene; 2,6-diaminotoluene; m-xylylenediamine; p-xylylenediamine; benzidine; 3,3'-dimethylbenzidine; 3,3'-dimethoxybenzidine; 1,5-diaminonaphthalene; bis(4-aminophenyl)methane; bis(4-aminophenyl)propane; bis(4-aminophenyl)sulfide; bis(4-aminophenyl)sulfone; bis(4-aminophenyl)ether; 4,4'-diaminodiphenylpropane; 4,4'-diaminodiphenylmethane(4,4'-methylenedianiline); 4,4'-diaminodiphenylsulfide; 4,4'-diaminodiphenylsulfone; 4,4'-diaminodiphenylether(4,4'-oxydianiline); 1,5-diaminonaphthalene; 3,3'dimethylbenzidine; 3-methylheptamethylenediamine; 4,4-dimethylheptamethylenediamine; 2,2',3,3'-tetrahydro-3,3,3',3'-tetramethyl-1,1'-spirobi[1H-indene]-6,6'-diamine; 3,3',4,4'-tetrahydro-4,4,4',4'-tetramethyl-2,2'-spirobi[2H-1-benzo- pyran]-7,7'-diamine; 1,1'-bis[1-amino-2-methyl-4-phenyl]cyclohexane, and isomers thereof as well as mixtures and blends comprising at least one of the foregoing. In an embodiment, the diamines are specifically aromatic diamines, especially m-and p-phenylenediamine and mixtures comprising at least one of the foregoing.

Suitable dianhydrides that can be used with the diamines include and are not limited to 2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride; 4,4'-bis(3,4-dicarboxyphenoxy) diphenylether dianhydride; 4,4'-bis(3,4-dicarboxyphenoxy) diphenylsulfide dianhydride; 4,4'-bis(3,4-dicarboxyphenoxy)benzophenone dianhydride; 4,4'-bis (3,4-dicarboxyphenoxy)diphenylsulfone dianhydride; 2,2-bis[4-(2,3-dicarboxyphenoxy) phenyl]propane dianhydride; 4,4'-bis(2,3-dicarboxyphenoxy) diphenylether dianhydride; 4,4'-bis(2,3-dicarboxyphenoxy)diphenylsulfide dianhydride; 4,4'-bis(2,3-dicarboxyphenoxy)benzophenone dianhydride; 4,4'-bis(2,3-dicarboxyphenoxy)diphenylsulfone dianhydride; 4-(2,3-dicarboxyphenoxy)-4'-(3,4-dicarboxyphenoxy)diphenyl-2,2-propane dianhydride; 4-(2,3-dicarboxyphenoxy)-4'-(3,4-dicarboxyphenoxy)diphenylether dianhydride; 4-(2,3-dicarboxyphenoxy)-4'-(3,4-dicarboxyphenoxy)diphenylsulfide dianhydride; 4-(2,3-dicarboxyphenoxy)-4'-(3,4-dicarboxyphenoxy)benzophenone dianhydride; 4-(2,3-dicarboxyphenoxy)-4'-(3,4-dicarboxyphenoxy)diphenylsulfone dianhydride; 1,3-bis(2,3-dicarboxyphenoxy)benzene dianhydride; 1,4-bis(2,3-dicarboxyphenoxy)benzene dianhydride; 1,3-bis(3,4-dicarboxyphenoxy)benzene dianhydride; 1,4-bis(3,4-dicarboxyphenoxy)benzene dianhydride; 3,3',4,4'-diphenyl tetracarboxylic dianhydride; 3,3',4,4'-benzophenonetetracarboxylic dianhydride; naphthalic dianhydrides, such as 2,3,6,7-naphthalic dianhydride, etc.; 3,3',4,4'-biphenylsulphonictetracarboxylic dianhydride; 3,3',4,4'-biphenylethertetracarboxylic dianhydride; 3,3',4,4'-dimethyldiphenylsilanetetracarboxylic dianhydride; 4,4'-bis (3,4-dicarboxyphenoxy) diphenylsulfide dianhydride; 4,4'-bis (3,4-dicarboxyphenoxy)diphenylsulphone dianhydride; 4,4'-bis (3,4-dicarboxyphenoxy)diphenylpropane dianhydride; 3,3',4,4'-biphenyltetracarboxylic dianhydride; bis(phthalic)phenylsulphineoxide dianhydride; p-phenylene-bis(triphenylphthalic)dianhydride; m-phenylene-bis(triphenylphthalic)dianhydride; bis(triphenylphthalic)-4,4'-diphenylether dianhydride; bis(triphenylphthalic)-4,4'-diphenylmethane dianhydride; 2,2'-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride; 4,4'-oxydiphthalic dianhydride; pyromellitic dianhydride; 3,3',4,4'-diphenylsulfonetetracarboxylic dianhydride; 4',4'-bisphenol A dianhydride; hydroquinone diphthalic dianhydride; 6,6'-bis(3,4-dicarboxyphenoxy)-2,2',3,3'-tetrahydro-3,3,3',3'-tetramethyl- -1,1'-spirobi[1H-indene]dianhydride; 7,7'-bis(3,4-dicarboxyphenoxy)-

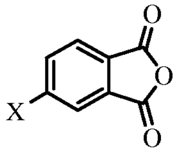
3,3',4,4'-tetrahydro-4,4,4',4'-tetramethyl- -2,2'-spirobi[2H-1-benzopyran]dianhydride; 1,1'-bis[1-(3,4-dicarboxyphenoxy)-2-methyl-4-phenyl]cyclohexane dianhydride; 3,3',4,4'-diphenylsulfonetetracarboxylic dianhydride; 3,3',4,4'-diphenylsulfidetetracarboxylic dianhydride; 3,3',4,4'-diphenylsulfoxidetetracarboxylic dianhydride; 4,4'-oxydiphthalic dianhydride; 3,4'-oxydiphthalic dianhydride; 3,3'-oxydiphthalic dianhydride; 3,3'-benzophenonetetracarboxylic dianhydride; 4,4'-carbonyldiphthalic dianhydride; 3,3',4,4'-diphenylmethanetetracarboxylic dianhydride; 2,2-bis(4-(3,3-dicarboxyphenyl)propane dianhydride; 2,2-bis(4-(3,3-dicarboxyphenyl)hexafluoropropane dianhydride; (3,3',4,4'-diphenyl)phenylphosphinetetracarboxylic dianhydride; (3,3',4,4'-diphenyl)phenylphosphineoxidetetracarboxylic dianhydride; 2,2'-dichloro-3,3',4,4'-biphenyltetracarboxylic dianhydride; 2,2'-dimethyl-3,3',4,4'-biphenyltetracarboxylic dianhydride; 2,2'-dicyano-3,3',4,4'-biphenyltetracarboxylic dianhydride; 2,2'-dibromo-3,3',4,4'-biphenyltetracarboxylic dianhydride; 2,2'-diiodo-3,3',4,4'-biphenyltetracarboxylic dianhydride; 2,2'-ditrifluoromethyl-3,3',4,4'-biphenyltetracarboxylic dianhydride; 2,2'-bis(1-methyl-4-phenyl)-3,3',4,4'-biphenyltetracarboxylic dianhydride; 2,2'-bis(1-trifluoromethyl-2-phenyl)-3,3',4,4'-biphenyltetracarboxylic dianhydride; 2,2'-bis(1-trifluoromethyl-3-phenyl)-3,3',4,4'-biphenyltetracarboxylic dianhydride; 2,2'-bis(1-trifluoromethyl-4-phenyl)-3,3',4,4'-biphenyltetracarboxylic dianhydride; 2,2'-bis(1-phenyl-4-phenyl)-3,3',4,4'-biphenyltetracarboxylic dianhydride; 4,4'-bisphenol A dianhydride; 3,4'-bisphenol A dianhydride; 3,3'-bisphenol A dianhydride; 3,3',4,4'-diphenylsulfoxidetetracarboxylic dianhydride; 4,4'-carbonyldiphthalic dianhydride; 3,3',4,4'-diphenylmethanetetracarboxylic dianhydride; 2,2'-bis(1,3-trifluoromethyl-4-phenyl)-3,3',4,4'-biphenyltetracarboxylic dianhydride, and all isomers thereof, as well as combinations of the foregoing.

Halo-displacement polymerization methods for making polyetherimides and polyetherimide sulfones include and are not limited to, the reaction of a bis(phthalimide) for formula (8):



(8),

wherein R is as described above and X is a nitro group or a halogen. Bis-phthalimides (8) can be formed, for example, by the condensation of the corresponding anhydride of formula (9):



(9),

wherein X is a nitro group or halogen, with an organic diamine of the formula (10):

$H_2N\text{-}R\text{-}NH_2$ (10),

wherein R is as described above.

Illustrative examples of amine compounds of formula (10) include: ethylenediamine, propylenediamine, trimethylenediamine, diethylenetriamine, triethylenetetramine, hexamethylenediamine, heptamethylenediamine, octamethylenediamine, nonamethylenediamine, decamethylenediamine, 1,12-dodecanediamine, 1,18-octadecanediamine, 3-methylheptamethylenediamine, 4,4-dimethylheptamethylenediamine, 4-methylnonamethylenediamine, 5-methylnonamethylenediamine, 2,5-dimethylhexamethylenediamine, 2,5-dimethylheptamethylenediamine, 2, 2-dimethylpropylenediamine, N-methyl-bis (3-aminopropyl) amine, 3-methoxyhexamethylenediamine, 1,2-bis(3-aminopropoxy) ethane, bis(3-aminopropyl) sulfide, 1,4-cyclohexanediamine, bis-(4-aminocyclohexyl) methane, m-phenylenediamine, p-phenylenediamine, 2,4-diaminotoluene, 2,6-diaminotoluene, m-xylylenediamine, p-xylylenediamine, 2-methyl-4,6-diethyl-1,3-phenylene-diamine, 5-methyl-4,6-diethyl-1,3-phenylene-diamine, benzidine, 3,3’-dimethylbenzidine, 3,3’–dimethoxybenzidine, 1,5-diaminonaphthalene, bis(4-aminophenyl) methane, bis(2-chloro-4-amino-3, 5-diethylphenyl) methane, bis(4-aminophenyl) propane, 2,4-bis(b-amino-t-butyl) toluene, bis(p-b-amino-t-butylphenyl) ether, bis(p-b-methyl-o-aminophenyl) benzene, bis(p-b-methyl-o-aminopentyl) benzene, 1, 3-diamino-4-isopropylbenzene, bis(4-aminophenyl) ether and 1,3-bis(3-aminopropyl) tetramethyldisiloxane. Mixtures of these amines can be used. Illustrative examples of amine compounds of formula (10) containing sulfone groups include but are not limited to, diamino diphenyl sulfone (DDS) and bis(aminophenoxy phenyl) sulfones (BAPS). Combinations comprising any of the foregoing amines can be used.

The polyetherimides can be synthesized by the reaction of the bis(phthalimide) (8) with an alkali metal salt of a dihydroxy substituted aromatic hydrocarbon of the formula HO-V-OH wherein V is as described above, in the presence or absence of phase transfer catalyst. Suitable phase transfer catalysts are disclosed in U.S. Patent No. 5,229,482. Specifically, the dihydroxy substituted aromatic hydrocarbon a bisphenol such as bisphenol A, or a combination of an alkali metal salt of a bisphenol and an alkali metal salt of another dihydroxy substituted aromatic hydrocarbon can be used.

In an embodiment, the polyetherimide comprises structural units of formula (5) wherein each R is independently p-phenylene or m-phenylene or a mixture comprising at least one of the foregoing; and T is group of the formula -O-Z-O- wherein the divalent bonds of the -O-Z-O- group are in the 3,3' positions, and Z is 2,2-diphenylenepropane group (a bisphenol A group). Further, the polyetherimide sulfone comprises structural units of formula (6) wherein at least 50 mole% of the R groups are of formula (4) wherein Q is $-SO_2-$ and the remaining R groups are independently p-phenylene or m-phenylene or a combination comprising at least one of the foregoing; and T is group of the formula -O-Z-O- wherein the divalent bonds of the -O-Z-O- group are in the 3,3' positions, and Z is a 2,2-diphenylenepropane group.

The polyetherimide and polyetherimide sulfone can be used alone or in combination with each other or with other of the disclosed polymeric materials in fabricating the polymeric components described herein. In an embodiment, only the polyetherimide is used. In another embodiment, the weight ratio of polyetherimide: polyetherimide sulfone can be from 99:1 to 50:50.

The polyetherimides can have a weight average molecular weight (Mw) of 5,000 to 100,000 grams per mole (g/mole) as measured by gel permeation chromatography (GPC). In some embodiments the Mw can be 10,000 to 80,000. The molecular weights as used herein refer to the absolute weight averaged molecular weight (Mw).

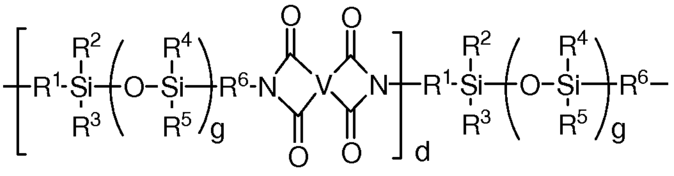
The polyetherimides can have an intrinsic viscosity greater than or equal to 0.2 deciliters per gram (dl/g) as measured in m-cresol at 25°C. Within this range the intrinsic viscosity can be 0.35 to 1.0 dl/g, as measured in m-cresol at 25°C.

The polyetherimides can have a glass transition temperature of greater than 180°C, specifically of 200°C to 500°C, as measured using differential scanning calorimetry (DSC) per ASTM test D3418. In some embodiments, the polyetherimide and, in particular, a polyetherimide has a glass transition temperature of 240 to 350°C.

The polyetherimides can have a melt index of 0.1 to 10 grams per minute (g/min), as measured by American Society for Testing Materials (ASTM) DI 238 at 340 to 370° C., using a 6.7 kilogram (kg) weight.

An alternative halo-displacement polymerization process for making polyetherimides, e.g., polyetherimides having structure (1) is a process referred to as the chloro-displacement process (X is Cl in formula (8)). The chloro-displacement process is illustrated as follows: 4-chloro phthalic anhydride and meta-phenylene diamine are reacted in the presence of a catalytic amount of sodium phenyl phosphinate catalyst to produce the bischloro phthalimide of meta-phenylene diamine (CAS No. 148935-94-8). The bischloro phthalimide is then subjected to polymerization by chloro-displacement reaction with the disodium salt of BPA in the presence of a catalyst in ortho-dichlorobenzene or anisole solvent. Alternatively, mixtures of 3-chloro- and 4-chlorophthalic anhydride may be employed to provide a mixture of isomeric bischloro phthalimides which may be polymerized by chloro-displacement with BPA disodium salt as described above.

Siloxane polyetherimides can include polysiloxane/polyetherimide block copolymers having a siloxane content of greater than 0 and less than 40 weight percent (wt%) based on the total weight of the block copolymer. The block copolymer comprises a siloxane block of Formula (I):



(I);

wherein R^{1-6} are independently at each occurrence selected from the group consisting of substituted or unsubstituted, saturated, unsaturated, or aromatic monocyclic groups having 5 to 30 carbon atoms, substituted or unsubstituted, saturated, unsaturated, or aromatic polycyclic groups having 5 to 30 carbon atoms, substituted or unsubstituted alkyl groups having 1 to 30 carbon atoms and substituted or unsubstituted alkenyl groups having 2 to 30 carbon atoms, V is a tetravalent linker selected from the group consisting of substituted or unsubstituted, saturated, unsaturated, or aromatic monocyclic and polycyclic groups having 5 to 50 carbon atoms, substituted or unsubstituted alkyl groups having 1 to 30 carbon atoms, substituted or unsubstituted alkenyl groups having 2 to 30 carbon atoms and combinations comprising at least one of the foregoing linkers, g equals 1 to 30, and d is 2 to 20. Commercially available siloxane polyetherimides can be obtained from SABIC Innovative Plastics under the brand name SILTEM* (*Trademark of SABIC Innovative Plastics IP B.V.)

The polyetherimide can have a weight average molecular weight (Mw) within a range having a lower limit and/or an upper limit. The range can include or exclude the lower limit and/or the upper limit. The lower limit and/or upper limit can be selected from 5000, 6000, 7000, 8000, 9000, 10000, 11000, 12000, 13000, 14000, 15000, 16000, 17000, 18000, 19000, 20000, 21000, 22000, 23000, 24000, 25000, 26000, 27000, 28000, 29000, 30000, 31000, 32000, 33000, 34000, 35000, 36000, 37000, 38000, 39000, 40000, 41000, 42000, 43000, 44000, 45000, 46000, 47000, 48000, 49000, 50000, 51000, 52000, 53000, 54000, 55000, 56000, 57000, 58000, 59000, 60000, 61000, 62000, 63000, 64000, 65000, 66000, 67000, 68000, 69000, 70000, 71000, 72000, 73000, 74000, 75000, 76000, 77000, 78000, 79000, 80000, 81000, 82000, 83000, 84000, 85000, 86000, 87000, 88000, 89000, 90000, 91000, 92000, 93000, 94000, 95000, 96000, 97000, 98000, 99000, 100000, 101000, 102000, 103000, 104000, 105000, 106000, 107000, 108000, 109000, and 110000 daltons. For example, the polyetherimide can have a weight average molecular weight (Mw) from 5,000 to 100,000 daltons, from 5,000 to 80,000 daltons, or from 5,000 to 70,000 daltons. The primary alkyl amine modified polyetherimide will have lower molecular weight and higher melt flow than the starting, unmodified, polyetherimide.

The polyetherimide can be selected from the group consisting of a polyetherimide, for example as described in US patents 3,875,116; 6,919,422 and 6,355,723 a silicone polyetherimide, for example as described in US patents 4,690,997; 4,808,686 a polyetherimide sulfone, as described in US patent 7,041,773 and combinations thereof, each of these patents are incorporated herein their entirety.

The polyetherimide can have a glass transition temperature within a range having a lower limit and/or an upper limit. The range can include or exclude the lower limit and/or the upper limit. The lower limit and/or upper limit can be selected from 100, 110, 120, 130, 140, 150, 160, 170, 180, 190, 200, 210, 220, 230, 240, 250, 260, 270, 280, 290, 300, and 310 degrees Celsius. For example, the polyetherimide can have a glass transition temperature (Tg) greater than about 200 degrees Celsius.

The polyetherimide can be substantially free (less than 100 ppm) of benzylic protons. The polyetherimide can be free of benzylic protons. The polyetherimide can have an amount of benzylic protons below 100 ppm. In an embodiment, the amount of benzylic protons ranges from more than 0 to below 100 ppm. In another embodiment, the amount of benzylic protons is not detectable.

The polyetherimide can be substantially free (less than 100 ppm) of halogen atoms. The polyetherimide can be free of halogen atoms. The polyetherimide can have an amount of halogen atoms below 100 ppm. In an embodiment, the amount of halogen atoms range from more than 0 to below 100 ppm. In another embodiment, the amount of halogen atoms is not detectable.

In an embodiment, the polyetherimides include a polyetherimide thermoplastic composition, comprising: (a) a polyetherimide, and (b) a phosphorus-containing stabilizer, in an amount that is effective to increase the melt stability of the polyetherimide, wherein the phosphorus-containing stabilizer exhibits a low volatility such that, as measured by thermogravimetric analysis of an initial amount of a sample of the phosphorus-containing stabilizer, greater than or equal to 10 percent by weight of the initial amount of the sample remains unevaporated upon heating of the sample from room temperature to 300° C. at a heating rate of a 20° C. per minute under an inert atmosphere. In an embodiment, the phosphorous-containing stabilizer has a formula $P\text{-}R_a$, where R' is independently H, alkyl, alkoxy, aryl, aryloxy, or oxy substituent and a is 3 or 4. Examples of such suitable stabilized polyetherimides can be found in U.S. Pat. No. 6,001,957, incorporated herein in its entirety.

The method can include a step of collecting the spun fiber on a forwarding or feeding roll without drawing the spun fiber. In the typical prior art process as depicted in Fig. 4, the convergence guide 406 collects the spun fibers and exerts a pull on the fibers while a series of drawing godets (collectively 409), usually operating at a higher speed, draw the fibers to reduce their denier. A finish material can be applied to the solidified fiber 407 by means of finish applicator in the form of a kiss roll 408. In the apparatus according to the present invention, the use of the finish and kiss roll 408 is optional, and the series of drawing godets 409, can be completely dispensed with in some embodiments. Therefore, the apparatus according to the invention comprises a spinneret according to Figs. 2 or 3, a forwarding or feeding roll to collect the spun fiber and at least one spool or bobbin upon which to collect the fine denier undrawn fiber for further use. The method can include a step of producing a solidified fiber from the melt spun polymer. Embodiments of the method can include a step of collecting the solidified fiber onto a spool without subjecting the solidified fiber to a drawing step. Embodiments of the method can produce the solidified fiber without a forced-air cooling step. The method can include a step of collecting the fiber onto the spool without any annealing step. The method can include a step comprises heating the spun fiber after it exits the spinneret.

The solidified fiber can have a dpf within a range having a lower limit and/or an upper limit. The range can include or exclude the lower limit and/or the upper limit. The lower limit and/or upper limit can be selected from 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2, 2.1, 2.2, 2.3, 2.4, 2.5, 2.6, 2.7, 2.8, 2.9, 3, 3.1, 3.2, 3.3, 3.4, 3.5, 3.6, 3.7, 3.8, 3.9, 4, 4.1, 4.2, 4.3, 4.4, 4.5, 4.6, 4.7, 4.8, 4.9 and 5 dpf. For example, according to certain preferred embodiments, the solidified fiber can have a dpf within a range from greater than 0 to 2.5 dpf.

The solidified fiber can have a shrinkage within a range having a lower limit and/or an upper limit. The range can include or exclude the lower limit and/or the upper limit. The lower limit and/or upper limit can be selected from 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2, 2.1, 2.2, 2.3, 2.4, 2.5, 2.6, 2.7, 2.8, 2.9, 3, 3.1, 3.2, 3.3, 3.4, 3.5, 3.6, 3.7, 3.8, 3.9, 4, 4.1, 4.2, 4.3, 4.4, 4.5, 4.6, 4.7, 4.8, 4.9 and 5 %. For example, according to certain preferred embodiments, the solidified fiber can have a shrinkage less than or equal to 2%.

An embodiment also relates to a new spinneret design suitable for using high viscosity amorphous engineering thermoplastics to make fibers having low deniers and low shrinkage. Unlike known processing of polyetherimide fibers, which requires the use of high pressure conditions (e.g., 1500 to 2000 psi), to maintain an even distribution of melt across spinneret holes, the spinnerets according to various embodiments are designed to enable even distribution at pressures as low as 400 psi (e.g., in the range of 400 to 1500 psi, preferably in the range of 400 to 1200 psi, most preferably in the range of 400-1000 psi). The die designs and spinnerets according permit melt spinning of amorphous thermoplastics, such as PEI into fine denier fibers. These embodiments can allow for full round melt channels throughout the die, minimize dead spaces or hang up areas where amorphous materials will collect or eddy and not flow easily and hang up and degrade, then intermittently release degraded materials into the melt stream. The length to diameter ratios of the melt channels can be optimized for amorphous materials, and the distribution channels can be designed to reduce the shear on the material and use the higher viscosity of the amorphous material in a melt state to get the even distribution of the melt across the spinneret. Using similar designs to the ones proposed, materials that were previously unable to be spun at all into fibers regardless of the denier, are able to be spun and wound onto spools, and the process optimized to achieve fine denier fibers.

One specific embodiment relates to a spinneret and/or a spin pack comprising a spinneret for producing an amorphous undrawn polyetherimide fiber of at most 2.5 dpf from a composition comprising an amorphous polyetherimide. The spinneret need not have distribution plates.

The spinneret can include a die having a plurality of round melt channels, wherein each round melt channel has a length and a diameter. The ratio of length:diameter of each round melt channel can be 1:1, 2:1, 3:1, 4:1, 5:1, 6:1, 7:1, 8:1, 9:1, 10:1, 11:1, or 12:1. For example, according to certain preferred embodiments, The ratio of length:diameter of each round melt channel can be from 2:1 to 6:1

According to an embodiment, the spinneret can operate at a reduced pressure compared to an identical spinneret comprising distribution plates. The operating pressure of a spinneret without distribution plates, according to various embodiments, can be reduced by a percentage relative to an identical spinneret comprising distribution plates. The percentage can be within a range having a lower limit and/or an upper limit. The range can include or exclude the lower limit and/or the upper limit. The lower limit and/or upper limit can be selected from 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59 and 60 %. For example, according to certain preferred embodiments, the operating pressure of a spinneret without distribution plates, according to various embodiments, can be reduced by a percentage of at least 40% relative to an identical spinneret comprising distribution plates.

The spinneret can further comprise at least one screen pack filter coupled to the die to distribute the composition to the die. The screen pack filter can have a mesh size within a range having a lower limit and/or an upper limit. The range can include or exclude the lower limit and/or the upper limit. The lower limit and/or upper limit can be selected from 100, 110, 120, 130, 140, 150, 160, 170, 180, 190, 200, 210, 220, 230, 240, 250, 260, 270, 280, 290, 300, 310, 320, 330, 340, 350, 360, 370, 380, 390, 400, 410, 420, 430, 440, 450, 460, 470, 480, 490 and 500 mesh. For example, according to certain preferred embodiments, the screen pack filter can have a US mesh size from 200 to 400 mesh.

Other embodiments relate to amorphous polymer fibers. The fibers can be drawn, but even in an undrawn state the fibers can have excellent properties.

An undrawn amorphous polymer fiber, according to various embodiments, can have a denier within a range having a lower limit and/or an upper limit. The range can include or exclude the lower limit and/or the upper limit. The lower limit and/or upper limit can be selected from 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2, 2.1, 2.2, 2.3, 2.4, 2.5, 2.6, 2.7, 2.8, 2.9, and 3. For example, according to certain preferred embodiments, the undrawn amorphous polymer fiber can have a denier less than 2.5.

An undrawn amorphous polymer fiber, according to various embodiments, can have a shrinkage within a range having a lower limit and/or an upper limit. The range can include or exclude the lower limit and/or the upper limit. The lower limit and/or upper limit can be selected from 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2, 2.1, 2.2, 2.3, 2.4, 2.5, 2.6, 2.7, 2.8, 2.9, 3, 3.1, 3.2, 3.3, 3.4, 3.5, 3.6, 3.7, 3.8, 3.9 and 4 %. For example, according to certain preferred embodiments, the undrawn amorphous polymer fiber can have a shrinkage from greater than 0 to less than or equal to 2%.

An undrawn amorphous polymer fiber, according to various embodiments, can have a polydispersity (Mw/Mn) within a range having a lower limit and/or an upper limit. The range can include or exclude the lower limit and/or the upper limit. The lower limit and/or upper limit can be selected from 1, 1.25, 1.5, 1.75, 2, 2.25, 2.5, 2.75, 3, 3.25, 3.5, 3.75, 4, 4.25, 4.5, 4.75, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, and 100. For example, according to certain preferred embodiments, the undrawn amorphous polymer fiber, according to various embodiments, can have a polydispersity (Mw/Mn) greater than or equal to 2.5

An undrawn amorphous polymer fiber, according to various embodiments, can have a denier within a range having a lower limit and/or an upper limit. The range can include or exclude the lower limit and/or the upper limit. The lower limit and/or upper limit can be selected from 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2, 2.1, 2.2, 2.3, 2.4, 2.5, 2.6, 2.7, 2.8, 2.9, 3, 3.1, 3.2, 3.3, 3.4, 3.5, 3.6, 3.7, 3.8, 3.9 and 4 . For example, according to certain preferred embodiments, an undrawn amorphous polymer fiber, according to various embodiments, can have a denier less than 2.2.

An undrawn amorphous polymer fiber, according to various embodiments, can have a strength within a range having a lower limit and/or an upper limit. The range can include or exclude the lower limit and/or the upper limit. The lower limit and/or upper limit can be selected from 1, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2, 2.1, 2.2, 2.3, 2.4, 2.5, 2.6, 2.7, 2.8, 2.9, 3, 3.1, 3.2, 3.3, 3.4, 3.5, 3.6, 3.7, 3.8, 3.9, 4, 4.1, 4.2, 4.3, 4.4, 4.5, 4.6, 4.7, 4.8, 4.9, 5, 10, 15, 20, 25, 30, 35, 40, 45 and 50 cN/dtex. For example, according to certain preferred embodiments, an undrawn amorphous polymer fiber, according to various embodiments, can have a strength of at least 2.6 cN/dtex.

An undrawn amorphous polymer fiber, according to various embodiments, can have the above identified properties while also being unannealed.

Another embodiment relates to article comprising the undrawn amorphous polyetherimide fiber. The article can include but is not limited to yarns made from the polyetherimide fiber (comprising i.e., one or more of the unannealed amorphous polyetherimide fiber optionally wound, braided, woven, spun, or otherwise associated with a different type of fiber), fabrics made from the undrawn amorphous fibers and/or yarns, and composites containing or based on fabrics made from the undrawn amorphous fibers. Examples of suitable composites include and are not limited to: papers, e.g., electrical papers, honeycomb papers, woven specialty papers, non-woven specialty papers; structural composites; and semi-structural composites.

In summary, a method comprising for the manufacture of a undrawn amorphous polymer fiber comprises extruding a melt through a spinneret under a pressure from 400 to 1500 psi (e.g., from 400 to 1000 psi) to produce a spun fiber, wherein the melt comprises an amorphous polymer composition, e.g., a polyetherimide, optionally wherein the amorphous polymer composition can have a melt flow rate from 4 to 18 g/10 min; collecting the spun fiber on a feeding roll without drawing the spun fiber, producing a solidified fiber from the spun fiber, wherein the solidified fiber has a dpf from greater than 0 to 2.5 dpf and the solidified fiber has a shrinkage less than or equal to 2%; and winding the solidified fiber onto a spool without subjecting the solidified fiber to a drawing step. In any of the foregoing embodiments, one or more of the following conditions can apply: the method can further optionally comprise collecting the fiber onto the spool without an annealing step; the method can further comprise heating the spun fiber after it exits the spinneret the solidified fiber is produced without a forced-air cooling step; the melt comprises one or more crystalline materials.

An amorphous polymer fiber, for example a fiber made by the foregoing method, has a denier less than 2.5, less than 2.2, or less than 2.0, and a shrinkage from greater than 0 to less than or equal to 2%; the fiber can further be a polyetherimide fiber, e.g., a polyetherimid optionally having a melt flow rate from 4 to 18 g/10 min, further optionally wherein the fiber has a polydispersity (Mw/Mn) greater than or equal to 2.5, and optionally a strength of at least 2.6 cN/dtex. The fiber can be unannealed. Articles comprising the foregoing fiber include yarns, fabrics, and composites.

A spinneret useful in the above method for producing an amorphous undrawn polyetherimide fiber (e.g., having a melt flow rate from 4 to 18 g/10 min) of at most 2.5 dpf has no distribution plates; and a die having a plurality of round melt channels, wherein each round melt channel has a length and a diameter, and wherein the ratio of length:diameter of each round melt channel is from 2:1 to 6:1, optionally wherein the spinneret operates at a pressure at least 40% less than an operating pressure of an identical spinneret comprising distribution plates, further optionally wherein the spinneret further comprises at least one screen pack filter coupled to the die to distribute the composition to the die, for example a filter having a US mesh size from 200 to 400 mesh.

The invention is further described in the following illustrative examples in which all parts and percentages are by weight unless otherwise indicated.

EXAMPLES

Table 1 lists materials employed in the examples.

Table 1

Name	Description	Source	Mw (Mw/Mn)
Polyetherimide A	Polyetherimide made under the trade name ULTEM 9011	SABIC	2

Two spinneret designs were employed in the examples. First, an Alpha Spinneret Design (See Figure 1) was employed. These types of spinneret designs will now be described in more detail. Second, a Beta Pack Spinneret Design (See Figures 2 and 3) according to various embodiments of the present invention was employed.

1. Description of Alpha Spinneret Design

As illustrated in Figure 1, a spin pack 100, according to the prior art, includes a capillary spinneret plate 102, which is a rectangular block that fits into a heater jacket area of an extruder with approximately 0.25 inch gap surrounding it. The prior art spin pack 100 requires a series of distribution plates 103 to be installed between a base plate 101 and the capillary spinneret plate 102. The distribution plates 103 are designed to provide both a pressure block to distribute the melt to the rectangular array of 144 capillaries evenly. The plates can be sized and shaped differently depending on the extruder being employed.

The distribution plates 103 are very thin, having a thickness of only about 0.02 inches, with a melt channel for the material being only 0.01 inches in diameter and 3/16 inches long. The restrictive dimensions of the melt channels create a severe flow condition for amorphous materials as well as high internal pack pressures. The internal pack pressures lead to a limited processing window with the materials. It also causes the material to plate out or to accumulate onto the face of capillary spinneret plate 102 during production. This residue builds up over time and has to be scraped off the face. This causes undesirable interruptions in the process.

Temperature control of the spin pack 100 is achieved through convective heating of the air gap space around the pack where it is installed in the extruder. Systems employing spin pack 100 are slow to respond to changes in operating conditions such as temperature and pressure. Additionally, a significant temperature loss from the set point to the spin pack is typically observed, requiring operators to adjust the set point temperature about 20 degrees Celsius over the desired temperature.

2. Description of New Spinneret Design (“Beta Pack Design”)

According to various embodiments a capillary spinneret for producing melt spun fibers from polyetherimides can resemble a shower head design, in that the capillary spinneret can have an array of capillaries distributed uniformly around a round pack face.

Figure 2 is a schematic diagram, illustrating a spin pack 200, according to various embodiments, having a capillary spinneret 201. The particular capillary spinneret 201 illustrated in Figure 2 has 72 capillaries 202, however any suitable number of capillaries can be employed. The capillary spinneret 201 can be sandwiched along with a distribution block 203 between a base plate 204 and an end cap 205. The distribution block 203 can have a plurality of distribution holes 206 for distributing a molten material to the capillary spinneret 201. The end cap 205 can have a plurality of through holes 207 alignable with corresponding holes 208 on the base plate 204 to secure and compress the spin pack 200 via bolts or other securing means.

Figure 3 is a schematic diagram, illustrating a spin pack 300, according to various embodiments, having a capillary spinneret 301. The particular capillary spinneret 301 illustrated in Figure 3 has 144 capillaries 315, however any suitable number of capillaries 315 can be employed. The capillary spinneret 301 can be sandwiched along with a screen pack filter 302, a first gasket 303, and a second gasket 304 between an end cap 305 and one or more base plates. As shown in Figure 3, a first base plate 306 and a second base plate 307 can be employed.

The end cap 305 can have a plurality of through holes 308 alignable with corresponding holes 309 on the first base plate 306 to secure and to compress a plurality of the components of the spin pack 200 via bolts or other securing means. The first base plate 306 can be secured to the second base plate 307 via bolts or other securing means inserted through through holes 310 on the first base plate 306 into receiving holes 311 on the second base plate 307.

The second base plate 307 can include an injection port 312, through which molten material can be injected into the spin pack 300, for example, from an extruder to which the spin pack 300 is secured via bolts or other securing means inserted through securing holes 313 on the second base plate 307. The first base plate 306 can include one or more distribution ports 314 to allow the molten material to continue flowing through the spin pack 300.

The examples described below employed a spin pack 300 as illustrated in Figure 3, because the capillary spinneret 301, having 144 capillaries resulted in a similar throughput as the old “Alpha” pack design.

The melt delivery to the pack face in this design has been simplified and streamlined. The distribution plates have been eliminated, and the distribution of the melt is accomplished via the screen pack filter 302 only. Distribution port 314 provides a full round runner system to bring the melt flow from the machine output to the center of the back side of the screen pack filter. The gaskets 303 and 304 can provide a sufficient cavity behind the filter 302 (i.e. on the side closest to first base plate 306) to allow for an even flow of material to build up behind the screen. Once sufficient pressure is built up behind the screen pack filter, the melt passes through and into the spinneret. It is then extruded via the pressure buildup through the capillaries 315 and drawn onto the take up rolls and wound onto one or more bobbins 410, as illustrated in Figure 4.

Figure 4 is a schematic diagram of a fiber process 400. A melt flow 401 from an extruder can be fed to a metering pump 402, through a filter 403, and through a spinneret 404. After exiting the spinneret 404, the melt flow 401 can be passed through an air quench 405. A convergence guide 406 can direct a fiber 407 to a finish applicator 408 and through a series of drawing godets 409 to be wound on one or more bobbins 410.

Various spinnerets were designed and constructed to allow for studying different length to diameter (L/D) ratios in the capillary hole, from 1 to 6, and diameters of 0.2 mm to 1.0 mm. Also screen pack filters ranging in mesh sizes from 200 to 400 mesh are used, depending on the material viscosity.

This spin pack design was mounted in a Hills GHP Bi-component Melt Spinning extrusion line. It was designed to fit into the same pack envelope that the Alpha design uses. The new design was configured to provide enough space around the head of the pack to allow direct contact temperature control with high wattage heater band. The new design provides much tighter and quicker thermal control over the spin pack face, a critical component in the melt spinning process.

Description of Making PEI with New Beta Spinneret Design

The material was dried at 300 degrees Fahrenheit for 4 to 8 hours to remove any moisture that would cause degradation of the polymer in a melt state.

The spin pack was assembled and placed in a preheat oven to bring it up to operating temperatures prior to installing into the machine and melt flow.

The machine was turned on and pre-heated for several hours before any material is introduced into the extruder. Once the temperatures are achieved, the pellets are fed into the extruder utilizing an automatic loader on the hopper above the extruder. The melt pump is turned on and then the extruder. These are manually controlled until both the melt stream is coming out of the machine, and a reasonable melt pressure and speed are achieved. Then the melt pressure is automatically controlled by pressure throughout the remainder of the process.

When the temperature and pressures reach a desired equilibrium, the pump and the extruder were stopped and the spinneret is removed from the oven and installed into the machine. The external heater band is mounted onto the spin pack along with its controlling thermocouple. This unit is then turned on and set to the desired set point.

The melt pump and extruder are then turned back on. The extruded fiber is collected in a waste barrel while the spinneret is brought up to operating temperatures. While this is happening, a melt sample is taken for the fiber, to determine the melt specific gravity.

Once the temperatures and pressures level out, the fiber is then pulled into the aspirator gun and collected onto the feeding or forwarding rolls below the optional spin finish kiss roll. The speed of the pump and the fowarding rolls define the diameter, or denier per filament (dpf) of the resultant fiber. Once the desired dpf is attained, the fiber is then loaded into the winder. The winder spools the fiber bundle onto at least one spool or a plurality of bobbins for later use in downstream processes.

For 2 dpf and lower denier PEI fibers, we run the pump from 4 to 6 rpm and the forwarding rolls at 1500 m/min to 2500 m/min. There is no need for stretching further on any draw rolls, or annealing on any relaxing rolls with this process configuration.

Description of Making PEI with Old Alpha Spinneret Design

The steps for the Alpha spinneret design are the same with respect to procedural steps to start up and run. The difference arises when you want to achieve 2 dpf or finer fibers. In this case it is necessary to stretch the fibers on draw rolls and attempt to control the shrinkage on a relax roll.

For 2 dpf PEI fibers using this set up, we run the melt pump between 5 and 7 rpm and the feed roll at 1500 m/min to 2500 m/min. The feed roll operating between 1500 m/min 2500 m/min, is maintained at a temperature of 200 degrees Celsius, the draw roll between 2250 m/min and 3000 m/min at a temperature of 200 degrees Celsius, and a relax roll between 2250 m/min and 3000 m/min also at a temperature of 200 degrees Celsius. The annealing of the fibers and the resulting shrinkage can be controlled by increasing the number of wraps on the godets and the temperature of the godets.

Techniques for Measuring the Denier of Fibers

The denier or linear density of the fibers is measured in accordance with the ASTM D1907-07 test method. The fiber was wound onto a reel 1 meter in circumference for a specified number of rotations and then weighed. The mass and length of the sample determine the linear density or Denier of the individual fiber filaments.

Techniques for Measuring the Shrinkage of Fibers

The testing for shrinkage of the fibers was performed in accordance with ASTM D2559 dry heat method. A sample of fibers of 1 meter in length is placed in an oven and exposed to an appropriate temperature for a predetermined amount of time. The sample is then removed from the oven the subsequent length is measured. Its deviation from its original 1 meter length determines its percent of change or shrinkage.

Example 1

The purpose of this example was to make PEI fibers in accordance to our invention. Fibers were made in accordance to the procedure described above, except that a 1 ¼ inch extruder and the Beta Pack design were employed. A 0.6 mm capillary spinneret was used with a 4 L/D and a 325 mesh screen pack filter were used.

A fiber was produced that had a dpf of 2 and a shrinkage of less than 2%. Unexpectedly, the fiber exhibited a combination of low denier and low shrinkage when produced directly from the spinneret without the need of stretching or annealing the fibers after initial take up. It was possible to make fibers at a rate of 1500 m/min to 2250 m/min for at least 2 hours without breaking. This example demonstrates that, advantageously, low denier fibers from polyetherimides having a molecular weight distribution of at least 2.5 can, therefore, be produced.

Example 2

The purpose of this example was to repeat the performance of the process in Example 1, and make polyetherimide fibers in accordance with various embodiments of the invention. Fibers were made in accordance to the procedure described above. A 0.6 mm capillary spinneret was used with a 4 L/D and a 325 mesh screen pack filter. The resulting fibers had a 1.8 dpf and a shrinkage of less than 2 %.

The resulting fibers exhibited a combination of low denier and low shrinkage when produced directly from the spinneret under low shear conditions without the need of stretching (drawing) or annealing the fibers. It was possible to make fibers at a rate of 1500 m/min to 2250 m/min for at least 2 hours without breaking. This example demonstrates that, advantageously, low denier fibers can be made from polyetherimides having a molecular weight distribution of at least 2.5.

Example 3

The purpose of this example was to make polyetherimide fibers in accordance to an embodiment of the invention while incorporating a lower mesh screen pack filter. Fibers were made in accordance to the procedure of Examples 1 and 2 except that a 200 US mesh screen pack filter was used.

The resulting fibers exhibited a combination of low denier and low shrinkage when produced directly from the spinneret under low shear conditions without the need of stretching or annealing the fibers. It was possible to make 2 dpf fibers with a shrinkage of 1.9%. These fibers were made at a rate of 1500 m/min to 2250 m/min for at least 2 hours without breaking. This example demonstrates that, advantageously, low denier fibers can be made from polyetherimides having a molecular weight distribution of at least 2.5.

Example 4

The purpose of this example was to make polyetherimide fibers in accordance to an embodiment of the invention while incorporating a lower mesh screen pack filter. Fibers were made in accordance to the procedure of Examples 1 and 2 except that a 400 mesh screen pack filter was used.

The resulting fibers exhibited a combination of low denier and low shrinkage when produced directly from the spinneret under low shear conditions without the need of stretching or annealing the fibers. It was possible to make 2 dpf fibers with a shrinkage of 1.8%. These fibers were made at a rate of 1500 m/min to 2250 m/min for at least 2 hours without breaking. This example demonstrates that, advantageously, low denier fibers can be made from polyetherimides having a molecular weight distribution of at least 2.5.

Example 5

The purpose of this example was to make polyetherimide fibers in accordance to an embodiment of the invention. Fibers were made in accordance to the procedure described in Example 4, except that a 2 L/D spinneret was used.

The resulting fibers exhibited a combination of low denier and low shrinkage when produced directly from the spinneret without the need of stretching or annealing the fibers. It was possible to make 2 dpf fibers with a shrinkage of less the 2%. These fibers were made at a rate of 1500 m/min to 2250 m/min for at least 2 hours without breaking. This example demonstrates that, advantageously, low denier fibers can be made from polyetherimides having a molecular weight distribution of at least 2.5.

Example 6

The purpose of this example was to repeat the performance of Example 5 and make PEI fibers in accordance to an embodiment of the invention.

The resulting fibers exhibited a combination of low denier and low shrinkage when produced directly from the spinneret under low shear conditions without the need of stretching or annealing the fibers. It was possible to make 2 dpf fibers with a shrinkage of less the 2%. These fibers were made at a rate of 1500 m/min to 2250 m/min for at least 2 hours without breaking. This example demonstrates that, advantageously, low denier fibers can be made from PEIs having a molecular weight distribution of at least 2.5.

Example 7

The purpose of this example was to make polyetherimide fibers in accordance to an embodiment of the invention. Fibers were made in accordance to the procedure described above, except that this example was run on the 1 inch screw with the Beta pack design. This set up used the 0.2 mm capillary with the L/D at 4 and a 200 mesh screen pack filter.

The resulting fibers exhibited a combination of low denier and low shrinkage when produced directly from the spinneret under low shear conditions without the need of stretching or annealing the fibers. It was possible to make 1.7 dpf fibers with a shrinkage of 1.1%. These fibers were made at a rate of 1500 m/min to 2250 m/min for at least 2 hours without breaking. The small capillary size resulted in an increase in pack pressure to 1400 psi, for this example. This example demonstrates that, advantageously, low denier fibers can be made from PEIs having a molecular weight distribution of at least 2.5.

Example 8

The purpose of this example was to make polyetherimide fibers in accordance to an embodiment of the invention. Fibers were made in accordance to the procedure described above, except that this example was performed on the 1 inch extruder using the Beta pack design. The spinneret was a 0.4 mm capillary diameter with an L/D ratio of 4. A 200 mesh screen pack filter was employed in this scenario as well.

The resulting fibers exhibited a combination of low denier and low shrinkage when produced directly from the spinneret under low shear conditions without the need of stretching or annealing the fibers. It was possible to make 2 dpf fibers with a shrinkage of 1.5%. These fibers were made at a rate of 1500 m/min to 2250 m/min for at least 2 hours without breaking. This example demonstrates that, advantageously, low denier fibers can be made from PEIs having a molecular weight distribution of at least 2.5.

Example 9 (Comparative)

The purpose of this example was to make polyetherimide fibers in accordance to prior art “Alpha” spin pack design, as illustrated in Figure 1, which contained distribution plates. Fibers were made in accordance to the procedure above and the following results were obtained. ULTEM ® 9011 PEI was used to make PEI Fibers. This example was run on the 1 inch extruder. The 0.6 mm capillary spinneret was used with a 4 L/D and a 325 mesh screen pack filter.

The results indicate that when PEI fibers were made in a high shear conditions, e.g. conditions where the pressure was more than or equal to 1400 psi, it was not possible to make PEI fibers that were undrawn and unannealed having the low shrinkage exhibited by fibers produced according to various embodiments of the invent. More particularly, in this example, fibers were produced at a 2.2 dpf and a shrinkage of 4%. In addition, to obtain fibers using the Alpha spin pack, it was necessary to draw the fibers and then anneal them to try to achieve 2 dpf. This process then causes the shrinkage to be higher than the process in accordance with various embodiments of the invention. Additionally, this example employed a high pack pressure of over 1500 psi as compared to the pressures in most of the previous examples, which were between 400 and 600 psi.

Table 2 provides a summary of the results obtained in Examples 1 – 9.

TABLE 2

Example	DPF (Denier per Filament)	Pressure (psi)	Draw Ratio	Shrinkage (%)
1	2	450	1:1	Less than or equal to 2
2	1.75	400	1:1	Less than or equal to 2
8	2	500	1:1	1.94
4	1.75	400	1:1	Less than or equal to 2
5	2	440	1:1	1.84
6	2	540	1:1	Less than or equal to 2
7	1.7	1400	1:1	1.1
8	2	650	V	1.5
9 (Comparative)	2.2	1577	1:1	4

Although the present invention has been described in considerable detail with reference to certain preferred versions thereof, other versions are possible. Therefore, the spirit and scope of the appended claims should not be limited to the description of the preferred versions contained herein.

The content of all papers and documents that are filed concurrently with this specification and which are open to public inspection are incorporated herein by reference.

All the features disclosed in this specification (including any accompanying claims, abstract, and drawings) may be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

CLAIMS

What is claimed is:

1. A method comprising:

extruding a melt through a spinneret under a pressure from 400 to 1500 psi to produce a spun fiber, wherein the melt comprises an amorphous polymer composition;

collecting the spun fiber on a feeding roll without drawing the spun fiber,

producing a solidified fiber from the spun fiber,

wherein the solidified fiber has a dpf from greater than 0 to 2.5 dpf,

wherein the solidified fiber has a shrinkage less than or equal to 2%; and

winding the solidified fiber onto a spool without subjecting the solidified fiber to a drawing step.

2. The method according to Claim 1, wherein the amorphous polymer composition has a melt flow rate from 4 to 18 g/10 min.

3. The method according to any one of Claims 1 or 2, wherein the pressure is from 400 to 1000 psi.

4. The method according to any one of Claims 1 to 3, further comprising collecting the fiber onto the spool without an annealing step.

5. The method according to any one of Claims 1 to 4, wherein the solidified fiber is produced without a forced-air cooling step.

6. The method according to any one of Claims 1 to 5, wherein the process further comprises heating the spun fiber after it exits the spinneret.

7. The method according to any one of Claims 1 to 6, wherein the melt comprises one or more crystalline materials.

8. The method according to any one of Claims 1 to 7, wherein the amorphous polymer composition comprises a polyetherimide.

9. An undrawn amorphous polymer fiber having a denier less than 2.5 and a shrinkage from greater than 0 to less than or equal to 2%.

10. The undrawn amorphous polymer fiber of Claim 9, wherein the polymer fiber is a polyetherimide fiber, wherein the fiber has a polydispersity (Mw/Mn) greater than or equal to 2.5.

11. The undrawn amorphous polyetherimide fiber of any one of Claims 9 to 10, wherein the fiber has a denier less than 2.2.

12. The undrawn amorphous polyetherimide fiber of any one of Claims 9 to 11, wherein the fiber has a strength of at least 2.6 cN/dtex.

13. The undrawn amorphous polyetherimide fiber of any one of Claims 9 to 12,

14. An article comprising the undrawn amorphous polyetherimide fiber of any one of Claims 9 to 13.

15. A spinneret for producing an amorphous undrawn polyetherimide fiber of at most 2.5 dpf from a composition comprising an amorphous polyetherimide, the spinneret comprising

no distribution plates; and

a die having a plurality of round melt channels, wherein each round melt channel has a length and a diameter, and wherein the ratio of length:diameter of each round melt channel is from 2:1 to 6:1.

16. The spinneret of Claim 15, wherein the spinneret operates at a pressure at least 40% less than an operating pressure of an identical spinneret comprising distribution plates.

17. The spinneret of any one of Claims 15 to 16, wherein the spinneret further comprises at least one screen pack filter coupled to the die to distribute the composition to the die.

18. The spinneret of Claim 17, wherein the screen pack filter has a US mesh size from 200 to 400 mesh.

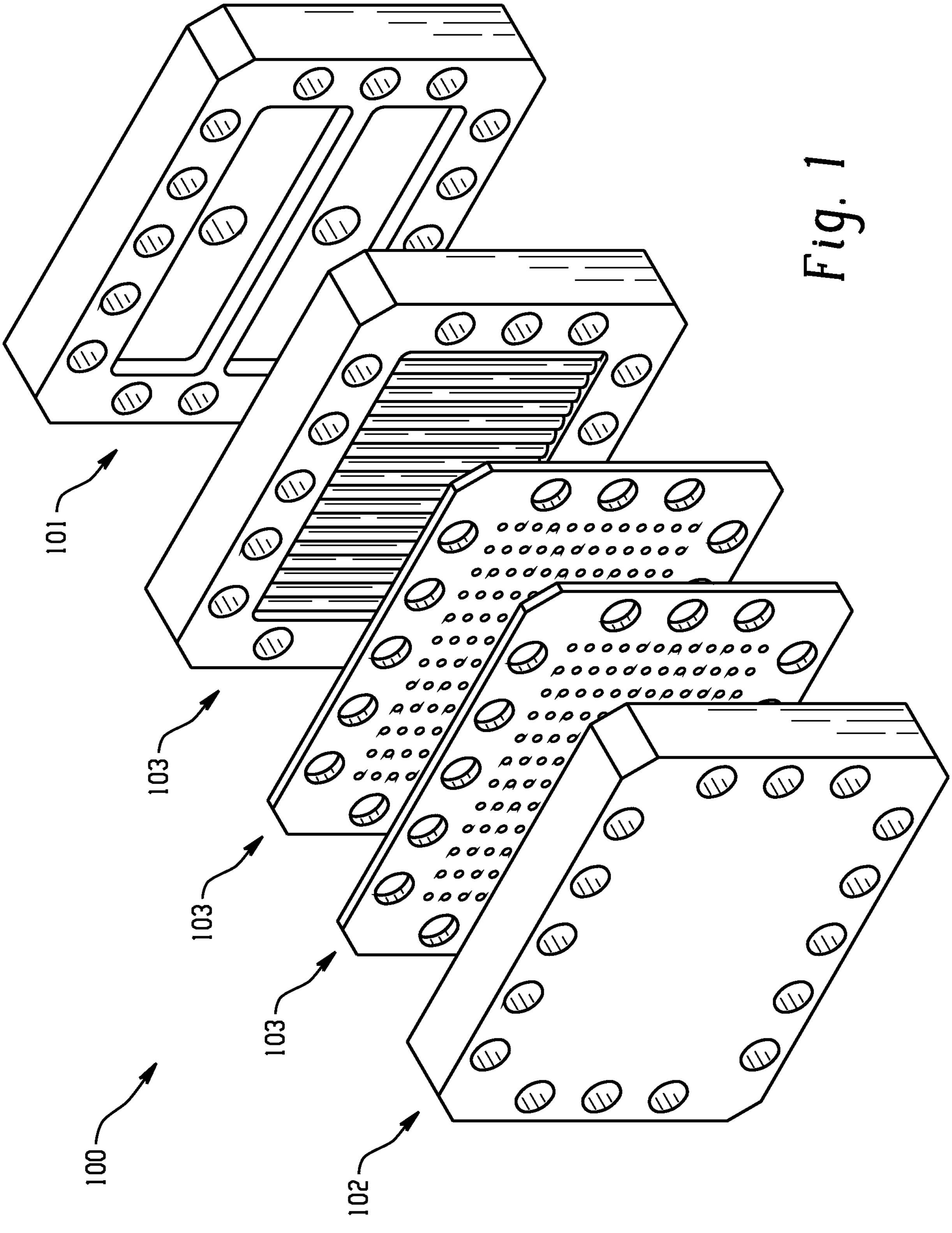


Fig. 1

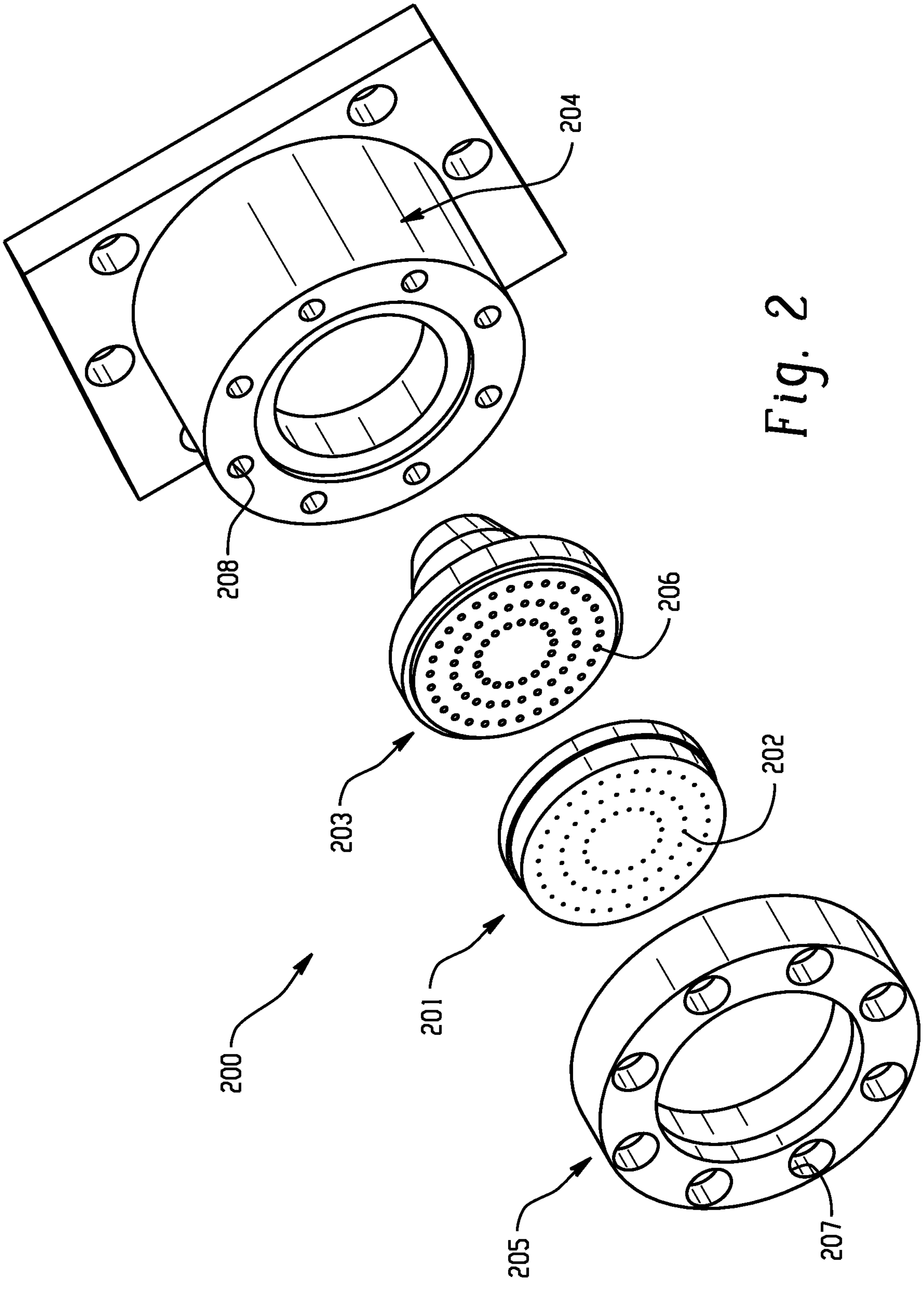


Fig. 2

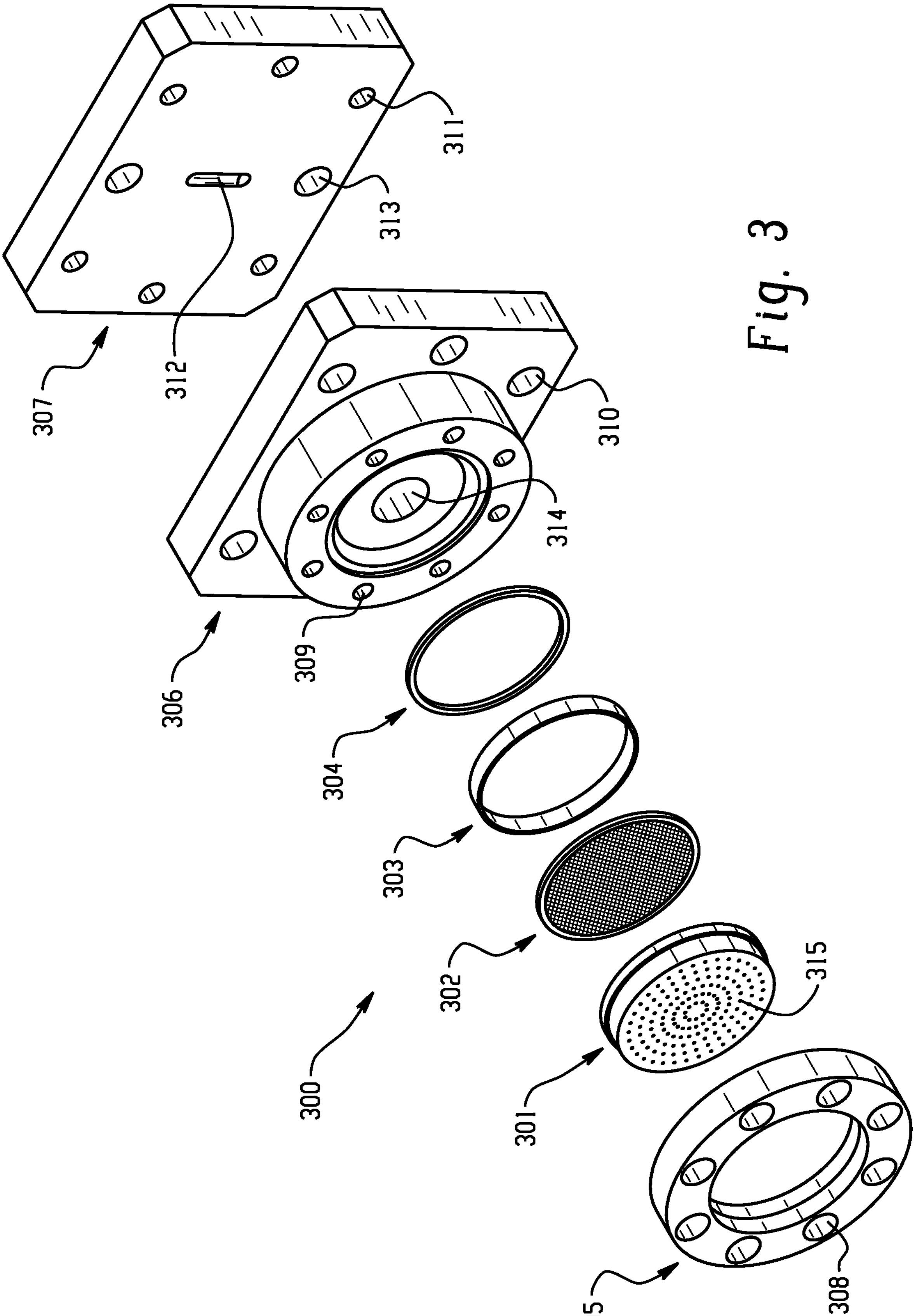


Fig. 3

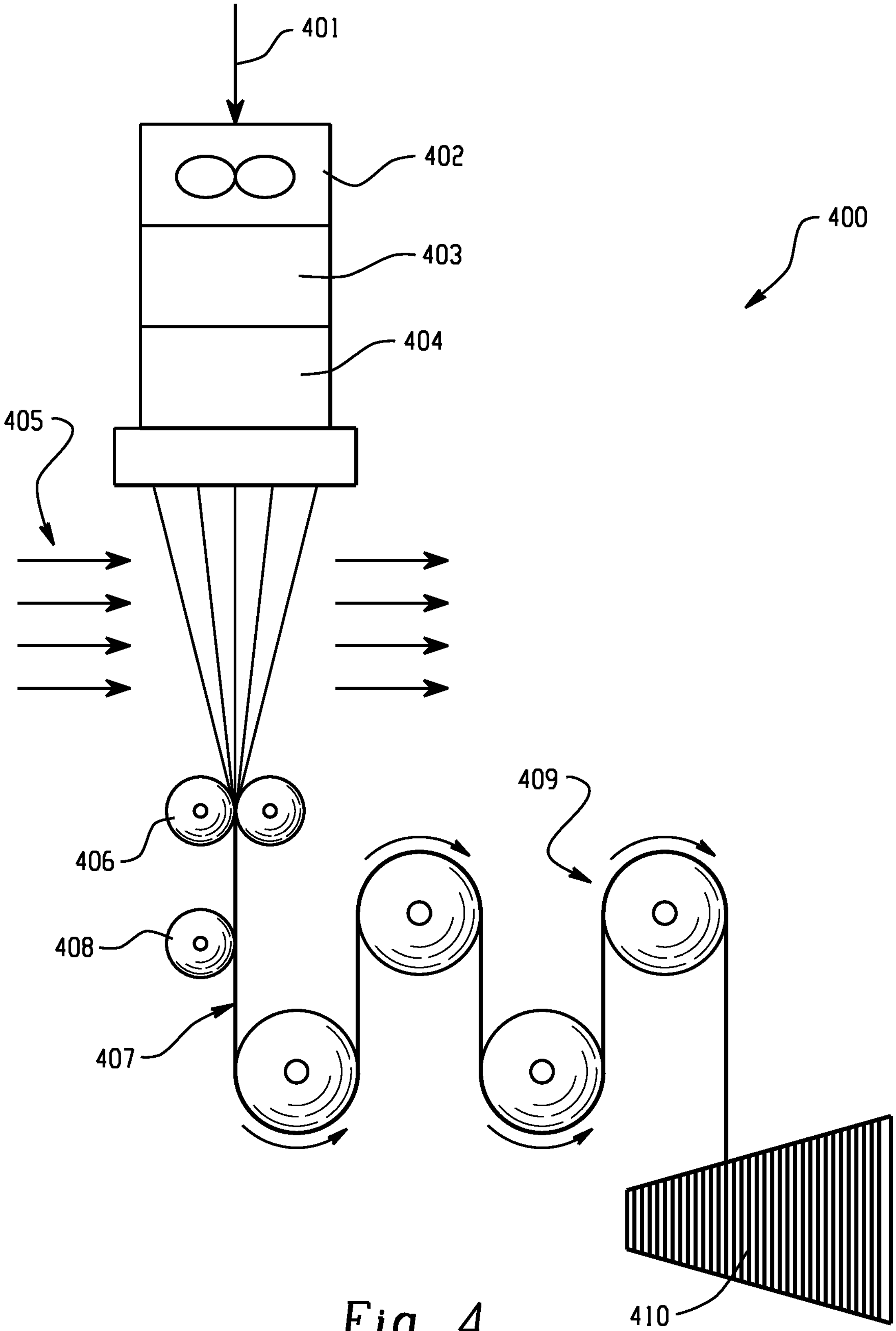


Fig. 4
PRIOR ART

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/052998

A. CLASSIFICATION OF SUBJECT MATTER
INV. D01D1/09 D01D4/06 D01D5/084 D01D5/098 D01F6/74
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
D01D D01F

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 2 412 850 A1 (KURARAY CO [JP]) 1 February 2012 (2012-02-01)	9-14
Y	examples 1,5	1-14
A	table 1 paragraphs [0032], [0035], [0037], [0047], [0062] -----	15-18
X	BOEHRINGER B ET AL: "NEW FILAMENTS AND FIBRES OF POLYETHERIMIDE", MAKROMOLEKULARE CHEMIE, MACROMOLECULAR SYMPOSIA, HUTHIG UND WEPF VERLAG. BASEL, CH, vol. 50, 1 October 1991 (1991-10-01), pages 31-39, XP000267605,	9,13,14
Y	paragraphs [02.2], [003.] -----	9-14
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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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International application No
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