US 20170191197A1

(19) United States

(12) Patent Application Publication

(10) Pub. No.: US 2017/0191197 A1

TALWAR et al.

(43) Pub. Date: Jul. 6, 2017

(54) **THERMALLY STABLE MELTBLOWN WEB COMPRISING MULTILAYER FIBERS**

(71) Applicant: **3M INNOVATIVE PROPERTIES COMPANY**, St. Paul, MN (US)

(72) Inventors: **Sachin TALWAR**, Woodbury, MN (US); **Torrence B. STAHL**, White Bear Lake, MN (US); **Eugene G. JOSEPH**, Blacksburg, VA (US)

(21) Appl. No.: **15/323,614**

(22) PCT Filed: **Jun. 11, 2015**

(86) PCT No.: **PCT/US2015/035334**

§ 371 (c)(1),
(2) Date: **Jan. 3, 2017**

Related U.S. Application Data

(60) Provisional application No. 62/017,864, filed on Jun. 27, 2014.

Publication Classification

(51) **Int. Cl.**

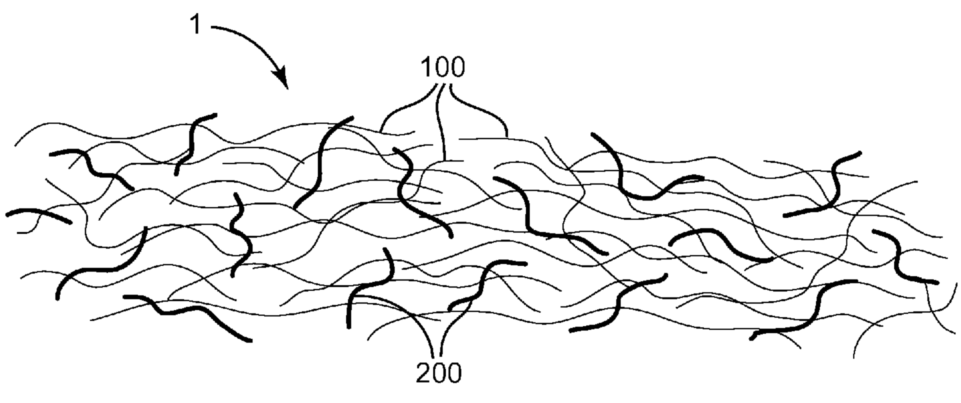
D04H 1/541	(2006.01)
D04H 1/559	(2006.01)
D01D 5/098	(2006.01)
D01D 5/30	(2006.01)
D01F 8/14	(2006.01)
D04H 1/56	(2006.01)
D04H 1/54	(2006.01)

(52) **U.S. Cl.**

CPC ***D04H 1/541*** (2013.01); ***D04H 1/56*** (2013.01); ***D04H 1/559*** (2013.01); ***D04H 1/54*** (2013.01); ***D01D 5/30*** (2013.01); ***D01F 8/14*** (2013.01); ***D01D 5/0985*** (2013.01); *D10B 2331/04* (2013.01)

(57) **ABSTRACT**

A thermally stable meltblown fibrous web, including a plurality of meltblown multilayer fibers, in which at least some of the meltblown multilayer fibers each include at least one primary layer that includes a primary polymer that is slow-crystallizing with a T_m of at least about 200° C., and at least one secondary layer that includes a secondary polymer that is fast-crystallizing with a T_m of at least about 200° C.



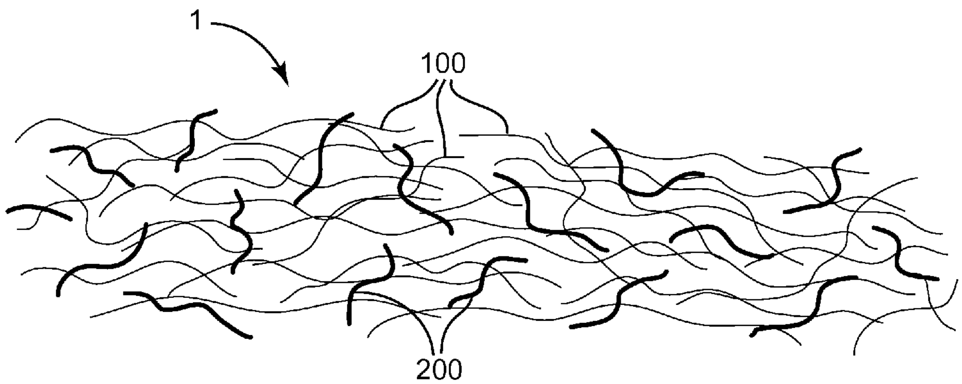


FIG. 1

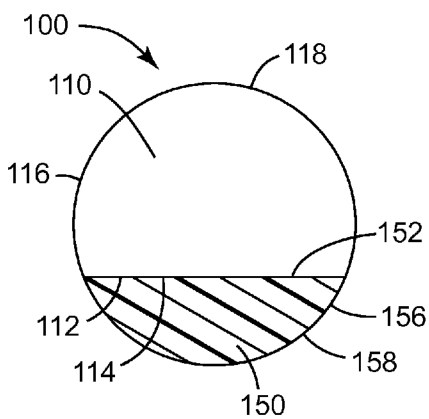


FIG. 2

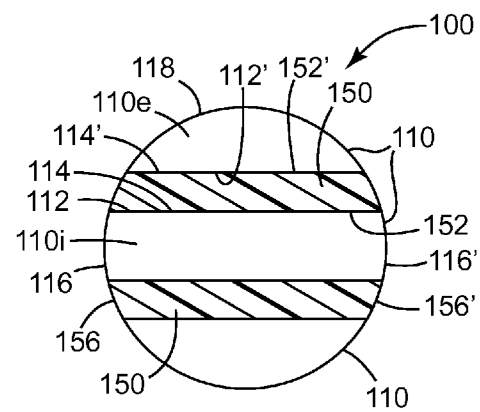


FIG. 3

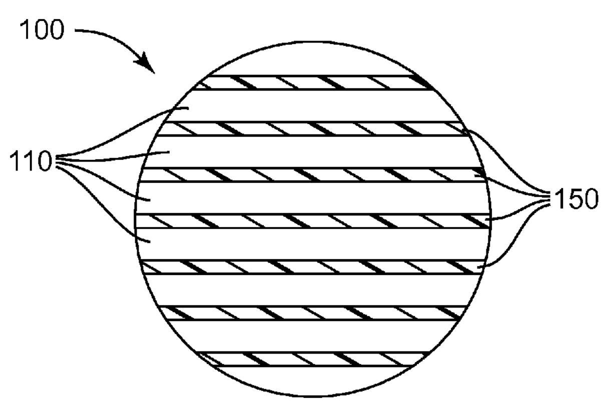


FIG. 4

THERMALLY STABLE MELTBLOWN WEB COMPRISING MULTILAYER FIBERS

BACKGROUND

[0001] Meltblowing is a process for forming nonwoven fibrous webs of thermoplastic polymeric fibers. In a typical meltblowing process, one or more molten polymer streams are extruded through die orifices and attenuated by convergent streams of high-velocity air ("blowing" air) to form fibers that are collected to form a meltblown nonwoven fibrous web. Meltblown nonwoven fibrous webs are used in a variety of applications, including acoustic and thermal insulation, filtration media, surgical drapes, and wipes, among others.

SUMMARY

[0002] In broad summary, herein is disclosed a thermally stable meltblown fibrous web, comprising: a plurality of meltblown multilayer fibers, wherein at least selected meltblown multilayer fibers each comprise at least one primary layer comprised of a primary polymer that is a slow-crystallizing polymer with a T_m of at least about 200° C., and at least one secondary layer comprised of a secondary polymer that is a fast-crystallizing polymer with a T_m of at least about 200° C. These and other aspects will be apparent from the detailed description below. In no event, however, should this broad summary be construed to limit the claimable subject matter, whether such subject matter is presented in claims in the application as initially filed or in claims that are amended or otherwise presented in prosecution.

BRIEF DESCRIPTION OF THE DRAWINGS

[0003] FIG. **1** is a side schematic cross-sectional view of a portion of an exemplary thermally stable meltblown fibrous web.

[0004] FIG. **2** is a cross-sectional slice view of an exemplary meltblown multilayer fiber.

[0005] FIG. **3** is a cross-sectional slice view of another exemplary meltblown multilayer fiber.

[0006] FIG. **4** is a cross-sectional slice view of another exemplary meltblown multilayer fiber.

[0007] Unless otherwise indicated, all figures and drawings in this document are not to scale and are chosen for the purpose of illustrating different embodiments of the invention. In particular the dimensions of the various components are depicted in illustrative terms only, and no relationship between the dimensions of the various components should be inferred from the drawings, unless so indicated. Like reference numbers in the various figures indicate like elements. Some elements may be present in multiples; in such cases only one or more representative elements may be designated by a reference number but it will be understood that such reference numbers apply to all such elements (in some cases, indicia (e.g., ') may be used for convenience of distinguishing multiple equivalent elements for purposes of description). Although terms such as "top", bottom", "upper", lower", "under", "over", "front", "back", "outward", "inward", "up" and "down", and "first" and "second" may be used in this disclosure, it should be understood that those terms are used in their relative sense only unless otherwise noted. In particular, for components that occur in equivalent multiples, the designation of "first" and "second" may apply to the order of description, as noted herein (with it being irrelevant as to which one of the components is selected to be described first).

[0008] As used herein as a modifier to a property or attribute, the term "generally", unless otherwise specifically defined, means that the property or attribute would be readily recognizable by a person of ordinary skill but without requiring absolute precision or a perfect match (e.g., within +/−20% for quantifiable properties). The term "substantially", unless otherwise specifically defined, means to a high degree of approximation (e.g., within +/−10% for quantifiable properties) but again without requiring absolute precision or a perfect match. Terms such as same, equal, uniform, constant, strictly, and the like, are understood to be within the usual tolerances or measuring error applicable to the particular circumstance rather than requiring absolute precision or a perfect match. Those of ordinary skill will appreciate that as used herein, terms such as "substantially no", "substantially free of", and the like, do not preclude the presence of some extremely low, e.g. 0.1% or less, amount of material, as may occur e.g. when using large scale production equipment subject to customary cleaning procedures.

Glossary

[0009] By a thermally stable web is meant a web exhibiting less than 10% thermal shrink when tested as described in the Examples herein.

[0010] By meltblown fibers/webs are meant fibers/webs prepared by meltblowing.

[0011] By meltblowing is meant extruding molten fiber-forming material through a plurality of orifices of a die to provide molten filaments. The filaments, essentially immediately after exiting the orifices, are contacted with high-velocity streams of gas (e.g., air) to attenuate the filaments into (meltblown) fibers, which are then collected, as described in detail later herein.

[0012] By "filaments" are meant molten streams of thermoplastic material that are extruded from a set of orifices; by fibers is meant solidified filaments. By web is meant a mass of collected fibers, at least some of which have been bonded to each other to a sufficient extent that web has sufficient mechanical integrity to be handled with conventional roll-to-roll equipment.

[0013] By T_m is meant the crystalline melting point of a semicrystalline polymer, measured as described in the Examples herein.

[0014] The terms fast-crystallizing and slow crystallizing as applied to a semicrystalline polymer, are defined and described in detail later herein.

[0015] By polymer is meant a material made of macromolecules having a number-average molecular weight of at least about 10,000. The term polymer is used for convenience of description and specifically encompasses copolymers, and also allows the presence of non-polymeric additives (as are often present in e.g. thermoplastic polymers for various purposes), unless otherwise indicated.

[0016] By non-polymeric means having a number-average molecular weight of below 10000.

[0017] By external is meant a layer, surface, or edge, that provides a radially outermost portion of a multilayer fiber.

DETAILED DESCRIPTION

[0018] Herein is disclosed a thermally stable meltblown nonwoven fibrous web **1**, as shown in exemplary embodiment in FIG. **1**. The web comprises a plurality of meltblown multilayer fibers **100**. By multilayer is meant that a fiber has at least two layers; specifically, at least one primary layer **110** comprised of a primary polymer, and at least one secondary 150 layer comprised of a secondary polymer. By multilayer is further meant that at least one of the primary layers **110**, and at least one of the secondary layers **150**, each comprise an external edge and/or a major external surface. The term multilayer fiber thus by definition specifically excludes so-called sheath-core fibers, in which a core layer does not comprise (except for e.g. sporadic statistical occurrences and defects) an external edge or major external surface.

[0019] An exemplary two-layer multilayer fiber **100** is shown in FIG. **2**, in cross-sectional slice view (viewed along a direction substantially aligned with the long axis of the multilayer fiber). Fiber **100** comprises primary polymer layer **110**, which comprises major external surface **118** and external edge **116** (in embodiments of this type, there may be no firm dividing line between the portion of layer **110** that is termed an major external surface and the portion that is termed an external edge), and further comprises major internal surface **112**. Fiber **100** further comprises secondary polymer layer **150**, which comprises major internal surface **152** and external edge **156**, and, in this embodiment, further comprises major external surface **158**. Major internal surface **152** of secondary polymer layer **150**, and major internal surface **112** of primary polymer layer **110**, are in direct contact with each other at internal interface **114**.

[0020] Another exemplary multilayer fiber **100** (in this case, a five-layer fiber) is shown in FIG. **3**, again in cross-sectional slice view. Exemplary five-layer fiber **100** of FIG. **3** comprises alternating primary and secondary layers, totaling three primary polymer layers **110** and two secondary polymer layers **150**. Each primary layer **110** comprises at least one major internal surface **112** at which it is direct contact with a major internal surface **152** of a secondary polymer layer **150** at an interface **114** (two such interfaces, and major internal surfaces of layers **110** and **150**, are identified in FIG. **3**, as **114** and **114'**, **112** and **112'**, and **152** and **152'**.) In multilayer fibers of this general type (e.g., with at least three primary layers **110** and at least two secondary layers **150**), at least one of the primary layers **110** will be an internal primary layer (designated as **110*i*** in FIG. **3**), meaning that such a primary layer is sandwiched between two secondary layers **150**. At least one other primary layer **110** may be an external primary layer (designated as **110*e*** in FIG. **3**), that comprises a major internal surface **112** that is in direct contact with a major internal surface **152** of a secondary layer **150** at an interface **114**, and that comprises another major surface that is a major external surface **118**. By definition, a primary layer **110** of a multilayer fiber will exhibit external edges **116** (two such edges, **116** and **116'**, are shown in FIG. **3**), a major external surface **118**, or both. While (as noted above) for e.g. multilayer fibers with few layers there may be no firm dividing line between a portion of a primary layer that is termed a major external surface and a portion that is termed an external edge, it will be appreciated that the more layers are present, the more readily external edges can be distinguished from major external surfaces (e.g., of an external primary layer). Again by definition, a secondary layer **150** of a multilayer fiber will exhibit an external edge **156** (two such edges, **156** and **156'**, are shown in FIG. **3**).

[0021] Still another exemplary multilayer fiber **100** (in this case, a fifteen-layer fiber) is shown in FIG. **4**, again in cross-sectional slice view. Exemplary fifteen layer fiber **100** of FIG. **4** comprises eight primary polymer layers **110** (six internal and two external) and seven secondary polymer layers **150**. In more general terms, a multilayer fibers can comprise at least n primary layers and at least n−1 secondary layers, at least n−2 of the secondary layers being individually sandwiched between a pair of primary layers, where n is a number between 3 and 51. (As used herein, individually sandwiched means that no other secondary layers are between the particular pair of primary layers.)

[0022] From the above descriptions it will be understood that multilayer fibers as defined herein exhibit at least one, and often several (e.g., five, ten or more) internal interfaces **114** between primary and secondary layers **110** and **150**, which internal interface(s) extend substantially along the long axis of the multilayer fiber in a predetermined and essentially uninterrupted manner. That is, in multilayer fibers as defined herein, the primary and secondary layers, and interfaces therebetween, are essentially continuous and extend along essentially the entire length of the multilayer fiber in an uninterrupted manner (except for such sporadic fluctuations, breaks, etc., as will be understood to be statistically present in any fiber made by a real-world meltblowing process). Thus, multilayer fibers as disclosed herein are by definition distinguished from monolayer fibers that contain blends of polymers (in which two polymer phases are distributed e.g. more or less in random fashion, e.g. with islands, globules, tendrils, etc., of one polymer phase being scattered among the other polymer phase). The ordinary artisan will understand that even though blended-polymer fibers may occasionally exhibit one polymer phase that extends along the long axis of the fiber to some extent, such unstable and unpredictable occurrences cannot be equated with a predetermined, multilayer fiber as disclosed herein.

[0023] In many embodiments, interfaces **114** between primary and secondary layers may be, on average, generally or even substantially planar (as in the depictions of FIGS. **2-4**). It is noted however that the depictions of FIGS. **2-4** are idealized and that in actuality the various layers, surfaces and interfaces may not necessarily be strictly planar at all locations, nor may fibers **100** necessarily be perfectly round in external shape. Furthermore, although a multilayer fiber of the general type having two primary layers **110** and one secondary layer **150** sandwiched therebetween is not shown in any figure, it is understood that the disclosures herein encompass such a configuration. Likewise, although no multilayer fiber having an even number of secondary layers, or a multilayer fiber having the same number of, or more, secondary layers as primary layers, is shown in these Figures, such arrangements are encompassed by the disclosures herein.

[0024] In at least some embodiments, primary layer(s) **110** and secondary layer(s) **150** are each monocomponent layers. By monocomponent layer is meant a layer that has essentially the same composition across the thickness, width, and length of the layer; a monocomponent layer may include additives and the like, as long as the composition is substantially uniform over the thickness, width and length of the fiber (except for such sporadic statistical fluctuations as the ordinary artisan will understand to be present in any real-world manufacturing process). In some embodiments, a primary polymer is the only polymeric component of primary layer **110**, and a secondary polymer is the only polymeric component of secondary layer **150**.

[0025] The average diameter of the meltblown multilayer fibers (measured e.g. by optical microscopy, using a sampling of representative fibers) may be in any desired range. It will be appreciated that meltblowing (because of e.g. the tendency of the high-velocity "blowing" air to reduce the diameter of the molten filaments), is particularly well-suited for the formation of so-called microfibers (meaning fibers with an average diameter of 10 microns or less). Thus, in various embodiments, the average diameter of the meltblown multilayer fibers may be less than about 30, 20, 15, 10, 5, 2, or 1 microns. In further embodiments, the average diameter of the meltblown multilayer fibers may be at least about 0.5, 1, 2, or 5 microns.

[0026] Multilayer fibers **100** are comprised of at least one primary layer **110** comprising a primary polymer with a T_m of at least about 200° C., and at least one secondary layer **150** comprising a secondary polymer with a T_m of at least about 200° C. By this is meant that both the primary polymer and the secondary polymer must be capable of exhibiting a crystalline melting point T_m (of at least about 200° C.) under at least some conditions. That is, such polymers must be capable of forming a significant number of crystalline domains (e.g., under conditions of sufficiently slow cooling); the terms primary polymer and secondary polymer do not encompass e.g. essentially amorphous polymers that will not form significant crystalline domains even if cooled very slowly and that thus are not capable of exhibiting a well-defined crystalline melting point. In various embodiments, the primary polymer may exhibit a T_m of at least about 210, 220, 230, 240, 250, or 260° C. In various embodiments, the secondary polymer may exhibit a T_m of at least about 210, 220, 230, 240, 250, or 260° C.

[0027] The primary polymer and the secondary polymer differ in that the primary polymer is a slow-crystallizing polymer and the secondary polymer is a fast-crystallizing polymer. In brief, by a fast-crystallizing polymer is meant a polymer that, under the relatively rapid cooling conditions employed in conventional meltblowing processes, forms crystalline domains at a rate sufficiently fast that the solidified meltblown fibers display a degree of crystallinity that is generally similar to the value that would be exhibited if the polymer were subjected to a slower cooling process. In contrast, by a slow-crystallizing polymer is meant a polymer that, under the cooling conditions employed in conventional meltblowing processes, forms crystalline domains at a rate that is sufficiently slow that the solidified meltblown fibers display a degree of crystallinity that is significantly below the value that would be exhibited if the polymer were subjected to a slower cooling process.

[0028] Polymers can be screened for the properties of slow-crystallizing and fast-crystallizing in the following manner. A polymer sample can be first subjected to a first heating step to and above the T_m, so as to erase any existing thermal history in the sample. This sample, with a standard heat history thus having been imposed on it, can then be subjected to slow cooling (which, for this purpose, can be taken as a cooling rate of 10° C. per minute). The sample is cooled to and well below the T_m (e.g., to room temperature). The sample is then subjected to a second heating step (e.g., at 10° C. per minute) up to and above the T_m. The heats of melting and cold crystallization are then calculated from data obtained from the second heating step and the degree of crystallinity (% crystallinity) is calculated therefrom. (The above measurements and calculations may be performed using any suitable differential scanning calorimetry (DSC) apparatus, using e.g. methods outlined in "DSC as Problem Solving Tool: Measurement of Percent Crystallinity of Thermoplastics", Perkin-Elmer (2000), which is incorporated by reference in its entirety herein.)

[0029] Another sample of the polymer can be likewise subjected to a first heating step to and above the T_m, so as to erase any existing thermal history in the polymer. This sample, with a standard heat history thus having been imposed on it, can then be subjected to fast cooling (which, for this purpose, can be taken as a cooling rate of 200° C. per minute). A second heating step can then be performed and the degree of crystallinity calculated for the rapidly-cooled sample in similar manner as discussed above.

[0030] The degree of crystallinity for the rapidly-cooled sample and the slowly-cooled sample can then be compared. A difference in degree of crystallinity of at least about 20% under rapidly-cooled conditions versus slowly-cooled conditions is indicative of a slow-crystallizing polymer. By way of a specific example, poly(ethylene terephthalate) (PET) is a prototypical slow-crystallizing polymer as defined herein. PET is capable of forming crystalline domains, and may often, e.g. after being slowly cooled from a melt, display a well-defined T_m in the range of about 250-260° C. and a degree of crystallinity in the range of e.g. 30 or 40% or more. However, if rapidly cooled from a melt e.g. as described above, PET may display a degree of crystallinity in the range of less than (often significantly less than) 30%.

[0031] Poly(butylene terephthalate), in contrast, is a prototypical fast-crystallizing polymer, which will typically display similar degrees of crystallization (e.g., within about 10% of each other) whether rapidly cooled or slowly cooled.

[0032] DSC screening as described above may be useful in identifying potentially useful primary and secondary polymers. However, for the purposes used herein, the most convenient method for identifying a semicrystalline polymer (assuming it meets the initial criteria of an identifiable T_m over 200° C.) as a primary polymer or a secondary polymer is to make a meltblown web that consists of monocomponent (non-multilayer) meltblown fibers of the polymer to be evaluated. This should be done using meltblowing process conditions (including, but not limited to, temperatures of the extruder, die and blowing air, volumetric rate and linear velocity of blowing air, die-to-collector distance, and so on, as will be well understood by the ordinary artisan) that are in conventional ranges for the meltblowing of that particular material. (Examples of conventional meltblowing conditions for certain polymers are found in the Examples herein.)

[0033] A monocomponent test web made in such a manner can then be subjected to a thermal shrinkage test as disclosed in the Examples herein. A polymer that, as a monocomponent meltblown web, displays a thermal shrinkage of less than 10%, is a secondary polymer as defined herein (again, as long as the other herein-disclosed criteria are met). In various embodiments, a secondary polymer may exhibit a thermal shrinkage of less than 8, 6, 4, or 2%. A polymer that, as a meltblown homopolymer web, displays a thermal shrinkage of 10% or greater, is a primary polymer as defined herein (again, as long as the other herein-disclosed criteria are met). In various embodiments, a primary polymer may exhibit a thermal shrinkage of greater than about 20, 30, 40, or even 50%.

[0034] Suitable primary polymers may be chosen from e.g. polyesters such as poly(ethylene terephthalate), poly (ethylene naphthalate), poly(trimethylene terephthalate) and at least some poly lactic acids that may exhibit a T_m over 200° C. (e.g., those with a relatively high content of D-lactide). Any desired combination of such primary polymers may be used. Suitable secondary polymers may be chosen from e.g. polyesters such as poly(butylene terephthalate), polyolefins such as polymethylpentene, and other polymers such as syndiotactic polystyrene, and any desired combination thereof.

[0035] The primary polymer and the secondary polymer may be present at a weight ratio of from about 95:5 to about 45:55 (primary:secondary), calculated based on the total weight of primary polymer and secondary polymer in the meltblown fibers of the web, including any polymer of either type that may be present in monocomponent meltblown fibers that are present in addition to the multilayer fibers, but not including any primary or secondary polymer that might be present in staple fibers. In various embodiments, the weight ratio of primary polymer to secondary polymer may be at least about 50:50, 60:40, 70:30, 75:25, 80:20, 85:15, or 90:10. In further embodiments, the weight ratio of primary polymer to secondary polymer may be at most about 90:10, 85:15, 80:20, 75:25, 70:30, 60:40, or 50:50.

[0036] As discussed in detail below, the arrangements disclosed herein allow the use of a relatively low amount (weight percentage) of secondary polymer, while achieving significant advantages over the performance that is possible with use of primary polymer alone. Such arrangements may be achieved in multilayer fibers e.g. by making the thickness of at least some of the secondary layers **150** (that is, the average distance between major surfaces **152** and **152'**, as shown in FIG. **3**), less than the thickness of at least some of the primary layers **110** (that is, the average distance between major surfaces **112** and **112'**, also as shown in FIG. **3**). In such manner, one or more secondary layers may be provided while minimizing the overall amount of secondary polymer used relative to the overall amount of primary polymer used. Thus in various embodiments, the ratio of the thickness of primary layer(s) **110** to that of secondary layer(s) **150** may be about 1.2:1, 1.5:1, 2:1, 3:1, or 4:1. (In such calculations, the thickness of an external layer (e.g., layer **110***e* of FIG. **3**) that has an arcuate major surface, can be taken to be the thickness of a rectangular area that has the same cross-sectional area as the external layer.)

[0037] It has been found that the inclusion of one or more secondary layers of fast-crystallizing secondary polymer seems able to significantly accelerate the crystallization of the slow-crystallizing primary polymer, even under such conditions of relatively rapid cooling as prevail in meltblowing. This can provide a solidified product comprising primary polymer with significantly increased crystallinity, and in consequence can provide a meltblown web that exhibits much lower thermal shrinkage than it would if it consisted of e.g. monocomponent fibers of primary polymer. Advantageously, this can be achieved while e.g. using fewer layers, and/or thinner layers, of secondary polymer, so that the overall weight ratio of secondary polymer to primary polymer can be maintained at a relatively low level, as noted above. This can provide significant benefits since such secondary polymers are often significantly more expensive than primary polymers.

[0038] Moreover, it has been found that the inclusion of one or more secondary polymers in the form of one or more layers as described herein, appears to be better able to accelerate the crystallization of a primary polymer than if the secondary polymer were intimately physically mixed with (e.g., melt-blended with) the primary polymer e.g. in the form of a polymer blend. This is a surprising result. The ordinary artisan would expect that the accelerating effect of a secondary polymer would be derived by way of the (rapidly-crystallized) surface of the secondary polymer providing nucleation sites for the primary polymer at the from the interface of the secondary polymer with the primary polymer. Therefore, it would be expected that mixing a secondary polymer with a primary polymer as a blend, which would be expected to disperse the secondary polymer among the primary polymer in the form of numerous parcels (ranging from e.g. tendrils or globules possibly down to macromolecular segments), would achieve a significantly higher surface area of secondary polymer among the primary polymer and would thus be much more effective in accelerating the crystallization of the primary polymer, in comparison to including secondary polymer in the form of layers as disclosed herein. However, the Working Examples presented herein show that, for a similar or even lower weight ratio of secondary polymer to primary polymer, multilayer meltblown fibers as disclosed herein appear to exhibit a lower thermal shrinkage than blended-polymer meltblown monolayer fibers. This is thus an unexpectedly advantageous result.

[0039] In some embodiments, web **1** may additionally include optional staple fibers **200**, as shown in exemplary embodiment in FIG. **1**. In web **1**, staple fibers **200** are distributed throughout, and intermingled within, the network of meltblown fibers. In various embodiments, staple fibers **200** may make up at least about 5, 10, 20, 30, or 40 wt. % of the total weight of the fibrous material (e.g. meltblown fibers plus staple fibers) of the web. In further embodiments, staple fibers **200** may make up at most about 60, 50, 40, 30, or 20 wt. % of the total weight of the fibrous material of the web.

[0040] Regardless of their particular process of manufacture or composition, staple fibers are typically machine cut to a specific predetermined or identifiable length and are added to a nonwoven web in solidified form. The length of the staple fibers often much less than that of meltblown fibers; and, in various embodiments, may be from about 1 to 8 cm or from about 2.5 cm to 6 cm. The average fiber diameter for the staple fibers is often greater than about 15 μm on average, and in various embodiments can be greater than 20, 30, 40, or 50 μm. Thus, in many embodiments the average fiber diameter of the staple fibers may be at least about 2, 4, or 8 times the average diameter of the meltblown multilayer fibers.

[0041] In some embodiments, the staple fibers may include synthetic polymeric materials. In some embodiments, the staple fibers may include natural fibers (chosen from fibers derived from e.g. bamboo, cotton, wool, jute, agave, sisal, coconut, soybean, hemp, and the like). If desired, the composition of at least some of the staple fibers may be chosen so that they can be meltbonded to each other and/or to the meltblown fibers during a molding process (such as might be used to form a shaped article that includes the meltblown web). Alternatively, they can be made of materials with properties (e.g. melting point) such that they do not bond to each other or to the meltblown fibers during a molding process.

[0042] Suitable staple fibers may be prepared e.g. from any suitable polyester and copolymers thereof, polyolefin such as e.g. polyethylene, polypropylene and copolymers thereof, polyamide, or combinations of any of these. The staple fibers may be crimped fibers e.g. like the fibers described in U.S. Pat. No. 4,118,531 to Hauser. Crimped fibers may have a continuous wavy, curly, or jagged profile along their length. The staple fibers may comprise crimped fibers that comprise e.g. about 10 to 30 crimps per cm. The staple fibers may be single component fibers or multicomponent fibers.

[0043] Various other components may be present in web **1** and in particular in meltblown multilayer fibers **100**, as desired for various purposes. For example, any desired type of particulate additive may be present in web **1**. In particular, if web **1** is used for filtration purposes, any suitable sorbent, catalytic, chemically reactive, etc. particulate additive may be present. Meltblown multilayer fibers **100**, in particular, may have any suitable ancillary components present therein. Such components may be present e.g. in the above-described primary polymer and/or the secondary polymer as obtained, and may include e.g. processing additives, antioxidants, UV stabilizers, fire-retardant additives, and so on. In some embodiments, the primary polymer may include one or more non-polymeric nucleating agents (e.g., melt additives), which may be chosen from e.g. various stearates, carboxylic acid salts, nitrogen-containing heteroaromatic compounds, and so on. However, in particular embodiments, the primary polymer includes less than about 5, 2, 1, or 0.5 wt. % of any non-polymeric nucleating agent. In specific embodiments, the primary polymer is substantially free of any non-polymeric nucleating agent.

[0044] In some further embodiments, web **1** may comprise at least some amount of polymeric nucleating agent, whether added in the form of separate layers of a multilayer fiber, or as blended (e.g. as a melt additive) with a primary or secondary polymer, etc. Such materials might include e.g. polyester-sulfonate salts, certain polyolefins such as polypropylene, polyethylene, and copolymers and blends thereof. It will be appreciated however that some such materials may exhibit a T_m of less than 200° C. and so cannot be considered to be a secondary polymer as disclosed herein. However, such materials may nevertheless provide benefits, as long as they are not present in such quantity as to unacceptably affect e.g. the thermal shrinkage of the resulting web. Thus, in various embodiments, multilayer fibers **100** may comprise up to, and no more than, about 5, 2, 1, or 0.5 wt. % of any polymeric nucleating agent. In specific embodiments, multilayer fibers **100** are substantially free of any polymeric nucleating agent.

[0045] In some embodiments it may be advantageous to minimize the amount of polymeric material that exhibits a T_m of less than 200° C. in the meltblown fibrous web. (In this context, the term polymeric material that exhibits a T_m of less than 200° C. specifically includes not merely homopolymer chains of the polymeric material, but any polymer segments of such material that may be present in a copolymer.) Thus, in various embodiments, any polymeric material with a T_m of less than 200° C., is present at less than about 20, 10, 5, 2, 1, or 0.5 wt. % based on the total fibrous material of the web (including e.g. staple fibers). In further embodiments, the meltblown fibrous web is substantially free of polymeric material with a T_m of less than 200° C. It may be helpful in some embodiments to minimize the amount of polymeric material that exhibits a T_m of less than 200° C., in particular in the meltblown fibers of the web. Thus, in various embodiments, any polymeric material with a T_m of less than 200° C., is present in the meltblown fibers of the web (including any non-multilayer meltblown fibers) at less than about 20, 10, 5, 2, 1, or 0.5 wt. %. In further embodiments, the meltblown fibers of the web are substantially free of polymeric material with a T_m of less than 200° C.

[0046] In various embodiments, web **1** as disclosed herein may exhibit a thermal shrink (measured as disclosed in the Examples herein) of less than about 10, 8, 6, 4, 2, or 1%. As discussed herein, such a property may provide significant advantages in certain applications.

[0047] As noted, the herein-disclosed nonwoven webs employ meltblown fibers, as defined above. The ordinary artisan will understand that a meltblowing process, and meltblown fibers and a meltblown nonwoven web formed by such a process, are distinguished from e.g. processes such as meltspinning and from the resulting products such as meltspun fibers and meltspun (e.g., spunbonded) nonwoven webs. The terms meltspinning and meltspun are terms of the art that refer to forming fibers by extruding molten filaments out of a set of orifices and allowing the filaments to cool and solidify to form fibers, with the filaments passing through an air space (which may contain streams of moving air) to assist in cooling the filaments. The cooled filaments are then passed through a drawing unit to at least partially draw the filaments (so as to e.g. induce orientation and enhanced physical properties). Meltspinning can thus be distinguished from meltblowing in that meltblowing involves the extrusion of molten filaments into converging high velocity air streams introduced by way of air-blowing openings (e.g., air knives) located in close proximity to (e.g., within 1 cm of) the extrusion orifices. The ordinary artisan will understand that meltblowing and meltspinning thus impart different characteristics (of e.g., molecular orientation and resulting physical properties) to the resulting fibers and webs (even if the fibers/webs are of like composition) and will thus appreciate that meltblown fibers and meltspun fibers can be readily distinguished from each other.

[0048] Thus, the herein-described meltblown fibers may be produced by the use of a meltblowing die capable of emitting molten multilayer filaments therefrom, a device for impinging high velocity "blowing" air on the molten multilayer filaments essentially immediately after they leave the orifices of the meltblowing die so as to attenuate the filaments into meltblown fibers, a collector for collecting the meltblown fibers, and various other equipment (e.g. extruders, temperature control equipment, and so on) as are customarily used in meltblowing.

[0049] Such an apparatus may be of the general type taught, for example, in van Wente, "Superfine Thermoplastic Fibers", *Industrial Engineering Chemistry*, Vol. 48, pages 1342 et sec (1956), or in Report No. 4364 of the Naval Research Laboratories, published May 25, 1954 entitled "Manufacture of Superfine Organic Fibers" by van Wente, A., Boone, C. D., and Fluharty, E. L. Such an apparatus can be modified for the specific purpose of producing multilayer meltblown fibers, and may include e.g. first and second extruders that respectively feed first and second flowstreams of molten polymer into a feedblock that combines the first and second flowstreams into a single, layered flowstream that is then distributed to multiple orifices. Methods and apparatus that may be used to produce multilayer meltblown fibers are discussed in further detail e.g. in U.S. Pat. Nos. 5,207,790 and 5,232,770 to Joseph. It will be clear that multilayer fibers made in this manner are distinguished from e.g. blended-polymer monolayer fibers in which two molten polymers are combined in a single extruder into a single blended flowstream and then extruded through common orifices. It will further be clear that multilayer fibers made in this manner are distinguished from sheath-core fibers in which a first molten polymer stream is extruded through a first, inner orifice, and a second molten polymer stream is extruded through a second orifice that annularly surrounds the inner orifice.

[0050] In some embodiments, the meltblown multilayer fibers may be collected on a flat surface (e.g., a porous collecting belt or netting) or on the surface of a single collecting drum. In other embodiments, the meltblown multilayer fibers may be collected in a gap between converging collecting surfaces, e.g. between first and second collecting drums. Such arrangements may provide that the meltblown fibers **100** are present in web **1** at least generally, or substantially, in a "C"-shaped cross-sectional configuration. Such arrangements (which are described in detail in U.S. Pat. No. 7,476,632 to Olson, which is incorporated by reference in its entirety herein), may provide e.g. increased loft and/or other beneficial properties.

[0051] In some embodiments, staple fibers may be optionally incorporated into the meltblown web as noted above. This may be performed e.g. by injecting an airborne stream of staple fibers into the airborne stream of attenuated filaments/fibers. (Since the process in which the molten filaments solidify to form fibers during their flight from the die orifices to the collector will be a statistical process, the terms filaments and fibers are somewhat interchangeable at this stage of the process.) This can form an intermingled airstream of multilayer meltblown fibers and staple fibers, which airstream can be impinged on a collector to collect the intermingled multilayer meltblown fibers and staple fibers as a mass of fibers. Apparatus and processes for injecting staple fibers into a stream of e.g. meltblown fibers are described in further detail in e.g. U.S. Pat. No. 7,989,371 to Angadjivand and in U.S. Pat. No. 4,118,531 to Hauser.

[0052] In some embodiments, at least some staple fibers may function as bonding fibers, as noted earlier. Alternatively, or as an adjunct to this, at least some of the meltblown fibers may (e.g., depending on the manner of collection and so on) be bonded, e.g. melt-bonded, to each other. If desired, any suitable post-bonding process might be used (e.g., point-bonding via a calendering operation, etc.).

[0053] The meltblown fibrous webs described herein can be incorporated (e.g., as a web, sheet, scrim, fabric, etc., of any suitable thickness, dimension, etc.) into articles such as thermal and acoustic insulating articles, liquid and gas filters made, and so on. Although any suitable use is envisioned, the resistance to thermal shrinkage of the meltblown web may render such articles particularly suitable for use in relatively high temperature environments. Such articles may find use in a wide variety of applications, e.g. acoustic and/or insulation of vehicles or of architectural components, in personal protective devices or clothing, and so on. Such meltblown webs may be particularly useful in thermal insulation articles and/or high temperature acoustical insulation articles, noting that in some uses (e.g., in automotive hoodliners), such an article may perform both functions. Meltblown fibrous web **1** may be combined with any desired additional layer (e.g., scrim, facing, and so on), as may be advantageous in forming a particular article. Web **1**, along with any such additional layers, may be processed (e.g., shaped, cut, and so on) to form an article of a particular configuration.

List of Exemplary Embodiments

[0054] Embodiment 1 is a thermally stable meltblown fibrous web, comprising: a plurality of meltblown multilayer fibers, wherein at least selected meltblown multilayer fibers each comprise at least one primary layer comprised of a primary polymer that is a slow-crystallizing polymer with a T_m of at least about 200° C., and at least one secondary layer comprised of a secondary polymer that is a fast-crystallizing polymer with a T_m of at least about 200° C., wherein the meltblown multilayer fibers exhibit an average weight ratio of the primary polymer to the secondary polymer of from about 45:55 to about 95:05 and wherein the thermally stable meltblown fibrous web exhibits a thermal shrink of less than about 10%.

[0055] Embodiment 2 is the web of embodiment 1, wherein the primary polymer exhibits a T_m of at least about 240° C. and wherein the secondary polymer exhibits a T_m of at least about 240° C. Embodiment 3 is the web of any of embodiments 1-2, wherein the meltblown fibers exhibit an average weight ratio of primary polymer to secondary polymer of from about 60:40 to about 90:10. Embodiment 4 is the web of any of embodiments 1-3, wherein the meltblown fibers exhibit an average weight ratio of primary polymer to secondary polymer of from about 70:30 to about 80:20. Embodiment 5 is the web of any of embodiments 1-4, wherein the primary polymer is a polyester chosen from the group consisting poly(ethylene terephthalate), poly(ethylene naphthalate), poly(lactic acid), poly(trimethylene terephthalate), and combinations thereof. Embodiment 6 is the web of any of embodiments 1-4, wherein the primary polymer is poly(ethylene terephthalate). Embodiment 7 is the web of any of embodiments 1-6, wherein the primary polymer is substantially free of a non-polymeric nucleating agent.

[0056] Embodiment 8 is the web of any of embodiments 1-7, wherein the secondary polymer is chosen from the group consisting of poly(butylene terephthalate), polymethylpentene, and syndiotactic polystyrene.

[0057] Embodiment 9 is the web of any of embodiments 1-8, wherein at least selected multilayer fibers each comprise at least one pair of primary layers with a secondary layer individually sandwiched therebetween. Embodiment 10 is the web any of embodiments 1-8, wherein at least selected multilayer fibers each comprise at least three primary layers and at least two secondary layers, with each secondary layer being individually sandwiched between a pair of primary layers. Embodiment 11 is the web of any of embodiments 1-8, wherein at least selected multilayer fibers each comprise at least five primary layers and at least four secondary layers, with each secondary layer being individually sandwiched between a pair of primary layers. Embodiment 12 is the web of any of embodiments 1-8, wherein at least selected multilayer fibers each comprise at least n primary layers and at least n−1 secondary layers, at least n−2 of the secondary layers being individually sandwiched between primary layers, where n is a number between 7 and 51.

[0058] Embodiment 13 is the web of any of embodiments 1-12, wherein the primary layers are monocomponent layers and wherein the secondary layers are monocomponent layers. Embodiment 14 is the web of any of embodiments 1-13, wherein the plurality of meltblown fibers collectively exhibit an average fiber diameter of less than about 10 micrometers.

[0059] Embodiment 15 is the web of any of embodiments 1-14, wherein the web further comprises staple fibers, the staple fibers making up from about 5 wt. % to about 50 wt. % of the total weight of the fibrous material of the web.

[0060] Embodiment 16 is the web of any of embodiments 1-15, wherein the web exhibits a thermal shrink of less than about 6%. Embodiment 17 is the web of any of embodiments 1-15, wherein the web exhibits a thermal shrink of less than about 2%.

[0061] Embodiment 18 is the web of any of embodiments 1-17, wherein the meltblown fibers of the web comprise no more than about 5 wt. % of any polymeric material that exhibits a T_m of less than 200° C. Embodiment 19 is the web of any of embodiments 1-17, wherein the meltblown fibers of the web are substantially free of any polymeric material with a T_m of less than 200° C.

[0062] Embodiment 20 is an article comprising the thermally stable meltblown fibrous web of any of embodiments 1-19, wherein the article is selected from the group consisting of a thermal insulation article, an acoustic insulation article, a fluid filtration article, or a combination thereof.

[0063] Embodiment 21 is the article of embodiment 20, wherein the article is an acoustic insulation article that exhibits a thermal shrink of less than about 5%.

[0064] Embodiment 22 is a method comprising: extruding molten multilayer flowstreams through orifices of a meltblowing die to form molten multilayer filaments; attenuating the molten multilayer filaments with high-velocity gaseous streams to form multilayer meltblown fibers; and, collecting the multilayer meltblown fibers as a mass of fibers, wherein at least selected multilayer meltblown fibers of the collected mass of fibers flowstreams each comprise at least one primary layer comprised of a molten primary polymer that is a slow-crystallizing polymer with a T_m of at least about 200° C., and at least one secondary layer comprised of a molten secondary polymer that is a fast-crystallizing polymer with a T_m of at least about 200° C.

[0065] Embodiment 23 is the method of embodiment 22 wherein the attenuated multilayer filaments form an airborne stream of multilayer meltblown fibers, and wherein the method further includes injecting an airborne stream of staple fibers into the airborne stream of multilayer fibers and collecting the intermingled multilayer meltblown fibers and staple fibers as a mass of fibers. Embodiment 24 is the method of any of embodiments 22-23 wherein the method further includes bonding at least some of the fibers of the mass of fibers to each other to form a thermally stable meltblown fibrous web.

[0066] Embodiment 25 is the web of any of embodiments 1-19 made by the method of any of embodiments 22-24. Embodiment 26 is the article of any of embodiments 20-21 made by the method of any of embodiments 22-24.

EXAMPLES

Test Methods

[0067] Thermal Shrinkage

[0068] The thermal shrinkage meltblown webs can be obtained using three 10 cm by 10 cm samples. The dimension of each specimen is measured in both the machine (MD) and cross direction (CD), before and after placement in a Fisher Scientific Isotemp Oven (or the equivalent) at 180° C. for 15 minutes. Shrinkage for each samples is calculated in the MD and CD by the following equation:

$$\text{Shrinkage} = \left(\frac{L_o - L}{L_o}\right) \times 100\%$$

where L_0 is the initial specimen length and L is the final specimen length. Average values of shrinkage are calculated and reported.

[0069] T_m (Crystalline Melting Point)

[0070] The T_m of a polymer sample can be obtained using a TA Instruments Q2000 Modulated Differential Scanning calorimeter (MDSC) or the equivalent. A specimen is weighed and loaded into a compatible aluminum pan. A first heat is applied to heat the sample to temperature that is above an estimated T_m of the sample; then, the sample is cooled at a sufficiently slow rate (e.g., 10° C. per minute) to allow crystallization to occur. After these preliminary heating/cooling steps, a second heat is applied at a heating rate of e.g. 10° C. per minute and the heat flows are observed. The crystalline melting point T_m can be obtained from the second heat data as the apex of a well-defined first-order melting peak (if such a peak exists), as will be well understood by the ordinary artisan.

Apparatus and Methods of Making Meltblown Webs

[0071] Meltblown webs were prepared using an apparatus and process similar to that described in Wente, Van A., "Superfine Thermoplastic Fibers" in *Industrial Engineering Chemistry*, Vol. 48, pages 1342 et seq. (1956), and in Report No. 4364 of the Naval Research Laboratories, published May 25, 1954 entitled "Manufacture of Superfine Organic Fibers" by Wente, Van. A. Boone, C. D., and Fluharty, E. L. The apparatus utilized an extruder that was equipped with a gear pump to control the polymer melt flow and distribute it to a meltblowing die having circular smooth surfaced orifices with a 5:1 length to diameter ratio. The orifices were arranged in linear fashion on the die face, at a spacing of 10 orifices per cm. An air-supply device (air knife) was provided at the die face, for impinging high velocity "blowing" air in a converging fashion on the molten filaments essentially immediately after the molten filaments exited the orifices of the meltblowing die.

[0072] For Working Example multilayer fibers, the apparatus was modified (in generally similar manner to that disclosed in Example 1 of U.S. Pat. No. 5,207,970) to include two extruders, each extruder having a gear pump so that the output of each extruder could be independently controlled, and each extruder configured to feed molten extrudate output to a splitter feedblock similar to that described in U.S. Pat. No. 3,480,502 to Chisholm and U.S. Pat. No. 3,487,505 to Shrenk. The splitter feedblock was configured to deliver the multilayer molten polymer stream to a meltblowing die generally as described above.

REPRESENTATIVE WORKING EXAMPLES

Working Example 1

[0073] A meltblown fibrous web comprising a plurality of meltblown multilayer fibers was made using the above-described apparatus and general method, operated as described below. The primary polymer was poly(ethylene terephthalate) (PET; 0.54 intrinsic viscosity) resin obtained from Nan Ya Plastics Corporation, America, Livingston, N.J. under the trade designation N211. The secondary polymer was poly(butylene terephthalate) (PBT) obtained from SABIC Innovative Plastics, Pittsfield, Mass. under the trade designation Valox-195-1001.

[0074] The first and second extruders respectively delivered the PET and PBT melt streams to the feedblock. The gear pumps were adjusted so that a 75:25 PET:PBT weight ratio of polymer melt was delivered to the feedblock and a 0.175 kg/hr/cm die width total polymer throughput rate was maintained at the meltblowing die. The die was held at approximately 305° C. and the feedblock was held at approximately 305° C.; the extruder melt temperature (proximal the discharge end of each extruder barrel) was held at approximately 305° C. and 270° C. for the first and second extruders, respectively. The air knife gap width of the blowing air supply device was approximately 0.76 mm; the temperature of the high velocity blowing air was maintained at a set point of approximately 400° C. and a pressure suitable to produce a uniform web. The melt streams were merged in an alternating fashion into a five layer melt stream on exiting the feedblock, with the first, third and fifth layers being PET and the second and fourth layers being PBT.

[0075] The thus-formed meltblown multilayer fibers were collected on an air-permeable belt at a DCD (die-to-collector distance) of approximately 38 cm. The thus-formed mass of fibers was found to exhibit sufficient mechanical integrity to serve as a self-supporting nonwoven web; no secondary bonding operation was performed. The meltblown multilayer fibers comprised five alternating layers (three primary layers of PET and two secondary layers of PBT). The meltblown multilayer fibers exhibited an average diameter of less than about 10 micrometers; the meltblown fibrous web had a basis weight of approximately 130 g/m^2.

Working Example 2

[0076] A meltblown fibrous web comprising a plurality of meltblown multilayer fibers was made in generally similar manner as in Working Example 1, except that the gear pumps were adjusted so that a 50:50 PET:PBT weight ratio of polymer melt was delivered. The die and feedblock were both held at approximately 280° C.; the melt temperatures of the first and second extruders were approximately 280° C. and 270° C., respectively. The temperature of the high velocity blowing air was maintained at a set point of approximately 390° C. The thus-formed meltblown multilayer fibers were collected at a DCD (die-to-collector distance) of approximately 30.5 cm. The meltblown multilayer fibers exhibited an average diameter of less than about 10 micrometers; the meltblown fibrous web had a basis weight of approximately 130 g/m^2.

Working Example 3

[0077] A meltblown fibrous web comprising a plurality of meltblown multilayer fibers was made in generally similar manner as in Working Example 1, except that the secondary polymer was polymethylpentene (PMP; obtained from Mitsui Chemicals, Rye Brook, N.Y. under the trade designation of TPX) rather than poly(butylene terephthalate). The primary:secondary polymer (PET:PMP) weight ratio was approximately 75:25 and a 0.14 kg/hr/cm die width total polymer throughput rate was maintained at the meltblowing die.

[0078] The die and feedblock were both held at approximately 300° C.; the melt temperatures of the first and second extruders were approximately 285° C. and 300° C., respectively. The temperature of the high velocity blowing air was maintained at a set point of approximately 400° C. The thus-formed meltblown multilayer fibers were collected at a DCD (die-to-collector distance) of approximately 15 cm. The meltblown multilayer fibers comprised five alternating layers (three primary layers of PET and two secondary layers of PMP). The meltblown multilayer fibers exhibited an average diameter of less than about 10 micrometers; the meltblown fibrous web had a basis weight of approximately 90 g/m^2.

Working Example 4

[0079] A meltblown fibrous web comprising a plurality of meltblown multilayer fibers was made in generally similar manner as in Working Example 3, except that the primary: secondary (PET:PMP) weight ratio was approximately 90:10.

Working Example 5

[0080] A meltblown fibrous web comprising a plurality of meltblown multilayer fibers was made in generally similar manner as in Working Example 3, except that the primary: secondary (PET:PMP) weight ratio was approximately 80:20.

Working Example 6

[0081] A meltblown fibrous web comprising a plurality of meltblown multilayer fibers was made in generally similar manner as in Working Example 3, except that the primary: secondary (PET:PMP) weight ratio was approximately 70:30.

Working Example 7

[0082] A meltblown fibrous web comprising a plurality of meltblown multilayer fibers was made in generally similar manner as in Working Example 3, except that the primary: secondary (PET:PMP) weight ratio was approximately 60:40.

[0083] The webs of Working Examples 4-7 exhibited a basis weight of approximately 90 g/m^2 and comprised meltblown multilayer fibers with an average diameter of less than about 10 micrometers.

Working Example 8

[0084] A meltblown fibrous web comprising a plurality of meltblown multilayer fibers was made in generally similar manner as in Working Example 3, except that the splitter feedblock was configured so that the multilayer fibers comprised seventeen alternating layers (eight primary layers of PET and nine secondary layers of PMP). The PET:PMP weight ratio was maintained at approximately 75:25. The die and feedblock were both held at approximately 300° C.; the melt temperatures of the first and second extruders were approximately 285° C. and 300° C., respectively. The temperature of the high velocity blowing air was maintained at a set point of approximately 400° C. The thus-formed meltblown multilayer fibers were collected at a DCD (die-to-collector distance) of approximately 15 cm.

Working Example 9

[0085] A meltblown fibrous web comprising a plurality of meltblown multilayer fibers was made in generally similar manner as in Working Example 3, except that the splitter feedblock was configured so that the multilayer fibers comprised two alternating layers (one primary layer of PET and one secondary layer of PMP). The PET:PMP weight ratio was maintained at approximately 75:25. The die and feedblock were both held at approximately 300° C.; the melt temperatures of the first and second extruders were approximately 285° C. and 300° C., respectively. The temperature of the high velocity blowing air was maintained at a set point of approximately 400° C. The thus-formed meltblown multilayer fibers were collected at a DCD (die-to-collector distance) of approximately 15 cm.

[0086] The webs of Working Examples 4-9 exhibited a basis weight in the range of approximately 90 g/m^2 and comprised meltblown multilayer fibers with an average diameter of less than about 10 micrometers.

COMPARATIVE EXAMPLES

Comparative Example 1

[0087] A meltblown nonwoven web was prepared using process conditions generally similar to that of Working Example 1, except that a splitter feedblock was not used and the meltblown fibers were all monolayer fibers consisting of a primary polymer, specifically poly(ethylene terephthalate) (PET; 0.54 intrinsic viscosity) resin obtained from Nan Ya Plastics Corporation, America, Livingston, N.J. under the trade designation N211.

[0088] The extruder gear pump was adjusted so to deliver the PET polymer melt at approximately 0.175 kg/hr/cm die width throughput rate. The die was held at approximately 305° C. and the feedblock was held at approximately 305° C.; the extruder melt temperature was held at approximately 305° C. The air knife gap width of the blowing air supply device was approximately 0.76 mm; the temperature of the high velocity blowing air was maintained at a set point of approximately 400° C. and a pressure suitable to produce a uniform web. The thus-formed meltblown monolayer fibers were collected at a DCD of approximately 38 cm.

Comparative Example 2

[0089] Shrinkage data was obtained from a meltblown nonwoven web in which all fibers were monolayer fibers consisting of a secondary polymer, specifically poly(butylene terephthalate) (PBT) available from SABIC Innovative Plastics, Pittsfield, Mass. under the trade designation Valox-195-1001. The process conditions were not obtained but it was believed that conventional (monolayer fiber) meltblowing apparatus and process conditions were employed. Also, the reported thermal shrink measurements for this material were obtained using a thermal shrink test (described in PCT Patent Application Serial No. PCT/CN2014/080901 to Chen et al., attorney docket number 75424WO003, entitled THERMALLY STABLE NONWOVEN WEB COMPRISING MELTBLOWN BLENDED-POLYMER FIBERS) that differed slightly from the above-described procedure. For example, the samples were held at 170° C. for 15 minutes rather than at 180° C. for 15 minutes. Accordingly, the shrinkage numbers for Comparative Example 2 may not precisely comparable to the other data; however, Comparative Example 2 is still useful in illustrating the general trends disclosed herein.

[0090] The thermal shrink for the various Working Examples and Comparative Examples is reported in Table 1.

TABLE 1

Sample	Composition	Total Layers	Thermal Shrink, %
Working Ex. 1	75:25 PET:PBT	5	6
Working Ex. 2	50:50 PET:PBT	5	4
Working Ex. 3	75:25 PET:TPX	5	1.0
Working Ex. 4	90:10 PET:TPX	5	1.5
Working Ex. 5	80:20 PET:TPX	5	1.8
Working Ex. 6	70:30 PET:TPX	5	0
Working Ex. 7	60:40 PET:TPX	5	0
Working Ex. 8	75:25 PET:TPX	17	0
Working Ex. 9	75:25 PET:TPX	2	7
Comparative Ex. 1	PET	1	52
Comparative Ex. 2	PBT	1	~6

OTHER WORKING EXAMPLES

[0091] The foregoing Examples are provided according to available records and have been provided for clarity of understanding only; no unnecessary limitations are to be understood therefrom. The tests and test results described in the Examples are intended to be illustrative rather than predictive, and variations in the testing procedure can be expected to yield different results. All quantitative values in the Examples are understood to be approximate in view of the commonly known tolerances involved in the procedures used.

[0092] It will be apparent to those skilled in the art that the specific exemplary elements, structures, features, details, configurations, etc., that are disclosed herein can be modified and/or combined in numerous embodiments. All such variations and combinations are contemplated by the inventor as being within the bounds of the conceived invention, not merely those representative designs that were chosen to serve as exemplary illustrations. Thus, the scope of the present invention should not be limited to the specific illustrative structures described herein, but rather extends at least to the structures described by the language of the claims, and the equivalents of those structures. Any of the elements that are positively recited in this specification as alternatives may be explicitly included in the claims or excluded from the claims, in any combination as desired.

Any of the elements or combinations of elements that are recited in this specification in open-ended language (e.g., comprise and derivatives thereof), are considered to additionally be recited in closed-ended language (e.g., consist and derivatives thereof) and in partially closed-ended language (e.g., consist essentially, and derivatives thereof). Although various theories and possible mechanisms may have been discussed herein, in no event should such discussions serve to limit the claimable subject matter. To the extent that there is any conflict or discrepancy between this specification as written and the disclosure in any document incorporated by reference herein, this specification as written will control.

What is claimed is:

1. A thermally stable meltblown fibrous web, comprising:

a plurality of meltblown multilayer fibers, wherein at least selected meltblown multilayer fibers each comprise at least one primary layer comprised of a primary polymer that is a slow-crystallizing polymer with a T_m of at least about 200° C., and at least one secondary layer comprised of a secondary polymer that is a fast-crystallizing polymer with a T_m of at least about 200° C.,

wherein the meltblown multilayer fibers exhibit an average weight ratio of the primary polymer to the secondary polymer of from about 45:55 to about 95:05 and wherein the thermally stable meltblown fibrous web exhibits a thermal shrink of less than about 10%.

2. The web of claim **1**, wherein the primary polymer exhibits a T_m of at least about 240° C. and wherein the secondary polymer exhibits a T_m of at least about 240° C.

3. The web of claim **1**, wherein the meltblown fibers exhibit an average weight ratio of primary polymer to secondary polymer of from about 60:40 to about 90:10.

4. The web of claim **1**, wherein the meltblown fibers exhibit an average weight ratio of primary polymer to secondary polymer of from about 70:30 to about 80:20.

5. The web of claim **1**, wherein the primary polymer is a polyester chosen from the group consisting poly(ethylene terephthalate), poly(ethylene naphthalate), poly(lactic acid), poly(trimethylene terephthalate), and combinations thereof.

6. The web of claim **1**, wherein the primary polymer is poly(ethylene terephthalate).

7. The web of claim **1**, wherein the primary polymer is substantially free of a non-polymeric nucleating agent.

8. The web of claim **1**, wherein the secondary polymer is chosen from the group consisting of poly(butylene terephthalate), polymethylpentene, and syndiotactic polystyrene.

9. The web of claim **1**, wherein at least selected multilayer fibers each comprise at least one pair of primary layers with a secondary layer individually sandwiched therebetween.

10. The web of claim **1**, wherein at least selected multilayer fibers each comprise at least three primary layers and at least two secondary layers, with each secondary layer being individually sandwiched between a pair of primary layers.

11. The web of claim **1**, wherein at least selected multilayer fibers each comprise at least five primary layers and at least four secondary layers, with each secondary layer being individually sandwiched between a pair of primary layers.

12. The web of claim **1**, wherein at least selected multilayer fibers each comprise at least n primary layers and at least n−1 secondary layers, at least n−2 of the secondary layers being individually sandwiched between primary layers, where n is a number between 7 and 51.

13. The web of claim **1**, wherein the primary layers are monocomponent layers and wherein the secondary layers are monocomponent layers.

14. The web of claim **1**, wherein the plurality of meltblown fibers collectively exhibit an average fiber diameter of less than about 10 micrometers.

15. The web of claim **1**, wherein the web further comprises staple fibers, the staple fibers making up from about 5 wt. % to about 50 wt. % of the total weight of the fibrous material of the web.

16. The web of claim **1**, wherein the web exhibits a thermal shrink of less than about 6%.

17. The web of claim **1**, wherein the web exhibits a thermal shrink of less than about 2%.

18. The web of claim **1**, wherein the meltblown fibers of the web comprise no more than about 5 wt. % of any polymeric material that exhibits a T_m of less than 200° C.

19. The web of claim **1**, wherein the meltblown fibers of the web are substantially free of any polymeric material with a T_m of less than 200° C.

20. An article comprising the thermally stable meltblown fibrous web of claim **1**, wherein the article is selected from the group consisting of a thermal insulation article, an acoustic insulation article, a fluid filtration article, or a combination thereof.

21. The article of claim **20**, wherein the article is an acoustic insulation article that exhibits a thermal shrink of less than about 5%.

22. A method comprising:

extruding molten multilayer flowstreams through orifices of a meltblowing die to form molten multilayer filaments;

attenuating the molten multilayer filaments with high-velocity gaseous streams to form multilayer meltblown fibers; and,

collecting the multilayer meltblown fibers as a mass of fibers,

wherein at least selected multilayer meltblown fibers of the collected mass of fibers flowstreams each comprise at least one primary layer comprised of a molten primary polymer that is a slow-crystallizing polymer with a T_m of at least about 200° C., and at least one secondary layer comprised of a molten secondary polymer that is a fast-crystallizing polymer with a T_m of at least about 200° C.

23. The method of claim **22** wherein the attenuated multilayer filaments form an airborne stream of multilayer meltblown fibers, and wherein the method further includes injecting an airborne stream of staple fibers into the airborne stream of multilayer fibers and collecting the intermingled multilayer meltblown fibers and staple fibers as a mass of fibers.

24. The method of claim **22** wherein the method further includes bonding at least some of the fibers of the mass of fibers to each other to form a thermally stable meltblown fibrous web.

* * * * *