

MELT-SPUN MULTIFILAMENT POLYOLEFIN YARN FORMATION PROCESSES AND YARNS FORMED THEREFROM

Background of the Invention

[001] Yarns and fibers formed from polyolefins can offer many desirable characteristics. For example, they can possess good tactile qualities such as hand feel, they can be resistant to degradation and erosion, and the raw materials can be easy to obtain as well as fairly inexpensive. As such, monofilament fibers as well as multifilament yarns have been formed from various polyolefins such as polypropylene. While the development of monofilament polyolefin fibers that have high modulus and high tenacity has been achieved, the ability to produce high modulus, high tenacity multifilament yarns of similar materials has not been as successful. As such, there remains room for improvement and variation within the art.

Summary of the Invention

[002] In one embodiment, the present invention is directed to a method of forming a polyolefin multifilament yarn. For example, the method can include forming a melted polymeric composition including a polyolefin, extruding the composition to form multiple filaments, quenching the filaments in a liquid bath, collecting the filaments to form a fiber bundle, and drawing the fiber bundle in a heated drawing step with a draw ratio greater than about 6, and in one embodiment, greater than about 10.

[003] The polyolefin can be any polyolefin suitable for forming yarn. For example, the polyolefin can be a copolymer. In one embodiment, the polyolefin can be a polypropylene. Optionally, the yarn can be formed of a mixture of two or more polyolefins. In one embodiment, the polyolefin can have a melt flow index between about 0.2 and about 50.

[004] In one embodiment, the polypropylene can contain a nucleating agent. For example, the nucleating agent can be a dibenzylidene sorbitol nucleating agent as is generally known in the art. Generally, the nucleating agent can be present in the melt in an amount less than about 1% by weight of the extruded composition, though this is not a requirement of the invention.

[005] The extruder can generally be any standard multi-orifice extruder. For example, the extruder can define multiple orifices, and each orifice can have a maximum cross-sectional dimension of between about 0.001 and about 0.050 inches.

[006] The melt can be extruded fairly slowly, for example between about 1 m/min and about 25 m/min into the liquid quench bath. Optionally, the bath can be heated, such as to a temperature of between about 50°C and about 130°C. In one embodiment, the surface of the quench bath can be quite close to the extruder orifices, for example within the distance of the die swell of the filaments. In another embodiment, the area immediately downstream of the orifice can be protected by a heated or an unheated gaseous shroud.

[007] The heated drawing step can be carried out in an oven, utilizing heated drawing rolls, or according to any other suitable heating method. Generally, the heated drawing step can be carried out at a temperature of between about 80°C and about 170°C. For example, the oven or the drawing rolls can be heated to the desired temperature. The heated drawing step can also be carried out at an even higher temperature if, for example, the yarn is exposed to the heat for a very short period of time.

[008] Other processes can also be carried out in forming the disclosed multifilament yarn such as one or more of the following: application of a lubricant, a second draw, or heat setting of the yarn.

[009] In another embodiment, the invention is directed to yarn that can be formed according to the disclosed processes. For instance, the yarn can include multiple filaments that can each describe a denier of less than about 300, in one embodiment each filament can have a denier of between about 0.5 and about 100. The yarn can have a high modulus, for instance greater than 40 g/d. In another embodiment, the yarn can have a modulus greater than 100 g/d, or greater than 150 g/d in some embodiments. The yarn can also have a high tenacity, for example greater than about 5 g/d in some embodiments, and greater than about 7 g/d in other embodiments. The disclosed yarns can also be fairly resistant to stretching, for example, the yarn can exhibit an elongation of less than about 10%.

[0010] The disclosed yarn is also believed to possess a crystalline structure

that is unique for multifilament polyolefin yarn. For instance, at least one of the filaments in the yarn can possess greater than 80% crystallinity, according to known wide-angle x-ray scattering (WAXS) measuring techniques. In one embodiment, at least one of the filaments in the yarn can have a ratio of equatorial intensity to meridonal intensity greater than about 1.0, which can be obtained from known small angle x-ray scattering (SAXS) measuring techniques. In another embodiment, the ratio of equatorial intensity to meridonal intensity can be greater than about 3.0.

[0011] In one embodiment, the invention is directed to secondary products that can be formed and can include the disclosed yarns. For example, the disclosed yarn can be beneficially utilized in forming ropes, woven materials, and nonwoven materials.

[0012] In one embodiment, the disclosed yarn can be utilized in reinforcement materials, for instance reinforcement materials for use in reinforcing a hydratable cementitious composition. For example, a yarn formed according to the disclosed processes can be chopped into smaller pieces, generally less than about 5 inches, to form a reinforcement material. In one embodiment, the yarn can be chopped into pieces of less than about 3 inches in length. In another embodiment, it can be chopped into pieces of less than about 1 inch in length. Optionally, the reinforcement materials can be degraded and/or deformed in addition to being cut into smaller pieces.

[0012a] One aspect of the present invention provides a method comprising: forming a melted polymeric composition comprising at least one polyolefin; extruding the melted polymeric composition through multiple orifices to form multiple filaments of the polymeric composition; quenching the filaments in a liquid bath; collecting the filaments to form a multifilament fiber bundle; and drawing the multifilament fiber bundle with a draw ratio greater than 6 to form a drawn multifilament yarn, wherein the multifilament fiber bundle is drawn while heated, the heat source being at a temperature of between 80°C and 170°C, and wherein at least one of said filaments has a ratio of equatorial intensity to meridonal intensity greater than 3.0 according to SAXS measuring techniques.

[0012b] Another aspect of the present invention provides a method of forming a multifilament yarn comprising:
forming a melted polymeric composition comprising a polypropylene having a melt flow index of between 2 and 50 ,

extruding the melted polymeric composition through multiple orifices at a rate of between 1 meter per minute and 25 meters per minute to form multiple filaments of the polymeric composition.

quenching the filaments in a heated liquid bath collecting the quenched filaments to form a multifilament fiber bundle, applying a lubricant to the fiber bundle and drawing the multifilament fiber bundle with a draw ratio greater than 6 to form a drawn multifilament yarn, wherein the multifilament fiber bundle is drawn while heated, the heat source being at a temperature of between 80°C and 170°C.

[0012c] A further aspect of the present invention provides a drawn multifilament yarn comprising at least three filaments, each filament including a polyolefin and each filament having a denier of less than 300 grams/9000 meters, the drawn multifilament yarn having been drawn at a draw ratio of greater than 6 and the drawn multifilament yarn having a modulus greater than 40 grams/denier wherein at least one of the filaments possesses greater than about 80% crystallinity according to WAXS measuring techniques.

[0012d] Yet another aspect of the present invention provides a reinforcement material comprising a yarn of a length of less than five inches, the yarn comprising at least three filaments each filament comprising a polyolefin and exhibiting a denier of less than 300 grams/9000 meters, the yarn having been drawn at a draw ratio of greater than 6 and having a modulus greater than 40 grams/denier, wherein the reinforcement material is for reinforcing a matrix material.

Brief Description of the Figures

[0013] A full and enabling disclosure of the present invention, including the best mode thereof, to one of ordinary skill in the art, is set forth more particularly in the remainder of the specification, including reference to the accompanying Figures in which:

[0014] Figure 1 illustrates one embodiment of a process according to the present invention;

[0015] Figure 2 illustrates the die swell of a single filament formed according to one embodiment of the present invention;

[0016] Figure 3 is the WAXS scattering pattern of a polypropylene filament pulled from a multifilament yarn formed according to one embodiment of the presently

disclosed processes; and

[0017] Figure 4 is the SAXS scattering pattern of the polypropylene filament of Figure 3.

[0018] Repeat use of reference characters in the present specification and drawings is intended to represent the same or analogous features or elements of the present invention.

Detailed Description of the Invention

[0019] Reference will now be made in detail to various embodiments of the invention, one or more examples of which are set forth below. Each embodiment is provided by way of explanation of the invention, not limitation of the invention. In fact, it will be apparent to those skilled in the art that various modifications and variations can be made in the present invention without departing from the scope or spirit of the invention. For instance, features illustrated or described as part of one embodiment, can be used in another embodiment to yield a still further embodiment. Thus, it is intended that the present invention cover such modifications and variations as come within the scope of the appended claims and their equivalents.

[0020] In general, the present invention is directed to multifilament polyolefin yarns and methods suitable for forming the disclosed multifilament polyolefin yarns. Beneficially, the disclosed methods can be utilized to form multifilament polyolefin yarns that can exhibit at least one of higher modulus or higher tenacity as compared to previously known multifilament polyolefin yarns.

[0021] The methods of the disclosed invention are generally directed to a melt-spinning yarn formation process. More particularly, the process utilized in forming the disclosed yarns can include forming a molten composition including a polyolefin, extruding multiple (i.e., at least three) individual filaments of the composition at a relatively low spinning rate, quenching the filaments in a liquid, forming a yarn structure of the multiple individual filaments, and mechanically drawing the yarn structure while the structure is heated.

[0022] In one particular embodiment, the polyolefin utilized in forming the disclosed yarns can be a polypropylene. This is not a requirement of the present invention, however, and though the ensuing discussion is generally directed toward

polypropylene, it should be understood that other polyolefins can optionally be utilized in the invention. For example, in one embodiment, the disclosed invention can be directed to the formation of polyethylene or polybutylene multifilament yarn.

[0023] In addition, and for purposes of this disclosure, the term polypropylene is intended to include any polymeric composition comprising propylene monomers, either alone (i.e., homopolymer) or in mixture or copolymer with other polyolefins, dienes, or other monomers (such as ethylene, butylene, and the like). The term is also intended to encompass any different configuration and arrangement of the constituent monomers (such as syndiotactic, isotactic, and the like). Thus, the term as applied to fibers is intended to encompass actual long strands, tapes, threads, and the like, of drawn polymer.

[0024] For purposes of this disclosure, the terms fiber and yarn are intended to encompass structures that exhibit a length that far exceeds their largest cross-sectional dimension (such as, for example, the diameter for round fibers). Thus, the term fiber as utilized herein differs from structures such as plaques, containers, sheets, and the like that are blow-molded or injection molded. Moreover, the term multifilament yarn is intended to encompass a structure that includes at least three filaments that have been individually formed such as, for example, via extrusion through a spinneret, prior to being brought in proximity to one another to form a single yarn structure.

[0025] One embodiment of the presently disclosed process generally 10 is schematically illustrated in Figure 1. According to the illustrated embodiment, a polymeric composition can be provided to an extruder apparatus 12. For example, in one embodiment, the polymeric composition can include polypropylene.

[0026] Generally, any polypropylene suitable for forming drawn yarn can be utilized in the disclosed process. For instance, polypropylene suitable for the present invention can generally be of any standard melt flow. For example, in one embodiment, standard extrusion grade polypropylene resin possessing ranges of melt flow indices (MFI) between about 0.2 and about 50 can be utilized in forming the disclosed multifilament yarns. In one embodiment, polypropylene possessing an MFI between about 0.5 and about 25 can be utilized. In one embodiment, the

polypropylene utilized in forming the multifilament yarn can have an MFI between about 1 and about 15.

[0027] In one embodiment, the polymeric composition provided to the extruder apparatus 12 can include polypropylene and a nucleating agent. According to this embodiment, the nucleating agent can generally be any material that can provide nucleation sites for the polypropylene crystals that can form during the transition of the polypropylene from the molten state to the solid structure. In one embodiment, the nucleating agent can exhibit high solubility in the polypropylene, though this is not a requirement of the invention. A non-limiting list of exemplary nucleating agents can include, for example, dibenzylidene sorbitol nucleating agents, as are generally known in the art, such as dibenzylidene sorbitol (DBS), monomethyldibenzylidene sorbitols such as 1,3:2,4-bis(p-methylbenzylidene) sorbitol (p-MDBS), dimethyl dibenzylidene sorbitols such as 1,3:2,4-bis(3,4-dimethylbenzylidene) sorbitol (3,4-DMDBS), and the like. Other suitable nucleating agents can include sodium benzoate, phosphate ester salts, such as NA-11 and NA-21, developed by Asahi Denka of Japan, or the hyper nucleating agents developed by Milliken Chemical of South Carolina such as, for example, Hyperform® HPN-68L.

[0028] According to the disclosed process, the polymeric composition, which can, in one embodiment include polypropylene combined with a nucleating agent, can be provided to an extruder apparatus 12. In this particular embodiment, the polypropylene component and the nucleating agent can be provided to the extruder apparatus 12 either separately or together, as at an inlet 13. For example, polypropylene and a nucleating agent can be provided to the extruder 12 either separately or together in liquid, powder, or pellet form. For instance, in one embodiment, both the polypropylene and the nucleating agent can be provided to the extruder 12 in pellet form at inlet 13. In another embodiment, the nucleating agent can be provided to the extruder apparatus 12 in a liquid form. For example, nucleating agents in a liquid form such as those disclosed in U.S. Patent 6,102,999 to Cobb, III, et al., which is incorporated herein by reference, can be utilized in the process.

[0029] When included, the nucleating agent can generally be present in the

mixture to be extruded in an amount less than about 1% by weight of the composition. For example, the nucleating agent can be present in the mixture in an amount less than about 0.5% by weight. In one embodiment, the nucleating agent can be present in the mixture in an amount between about 0.01% by weight and about 0.3% by weight. In another embodiment, the nucleating can be present in the mixture in an amount between about 0.05% by weight and about 0.25% by weight.

[0030] The mixture including the polypropylene and, optionally, the nucleating agent can also include various other additives as are generally known in the art. For example, in one embodiment, the disclosed multifilament yarn can be colored yarn, and the mixture can include suitable coloring agents, such as dyes or other pigments. According to this embodiment, it may be preferable to utilize a nucleating agent that will not affect the final color of the multi-component yarn, but this is not a requirement of the invention, and in other embodiments, nucleating agents can be utilized that enhance or otherwise affect the color of the formed yarn. Other additives that can be combined with the mixture can include, for example, one or more of anti-static agents, antioxidant agents, antimicrobial agents, adhesion agents, stabilizers, plasticizers, brightening compounds, clarifying agents, ultraviolet light stabilizing agents, surface active agents, odor enhancing or preventative agents, light scattering agents, halogen scavengers, and the like. In addition, additives can be included in the melt, or in some embodiments, can be applied as a surface treatment to either the undrawn fiber bundle or optionally to the drawn yarn, as generally known in the art.

[0031] In one embodiment, the extruder apparatus 12 can be a melt spinning apparatus as is generally known in the art. For example, the extruder apparatus 12 can include a mixing manifold 11 in which a composition including one or more polyolefins and any other desired additives can be mixed and heated to form a molten composition. The formation of the molten mixture can generally be carried out at a temperature so as to ensure melting of essentially all of the polypropylene. For example, in one embodiment, the mixture can be mixed and melted in a manifold 11 heated to a temperature of between about 175°C and about 325°C.

[0032] Optionally, to help ensure the fluid state of the molten mixture, in one embodiment, the molten mixture can be filtered prior to extrusion. For example, the

molten mixture can be filtered to remove any fine particles from the mixture with a filter of between about 180 and about 360 gauge.

[0033] Following formation of the molten mixture, the mixture can be conveyed under pressure to the spinneret 14 of the extruder apparatus 12, where it can be extruded through multiple spinneret orifices to form multiple filaments 9. For instance, the spinneret can define at least three spinneret orifices. In one embodiment, the spinneret can define between 4 and about 100,000 individual spinneret orifices. For purposes of this disclosure, the terms extrusion die and spinneret are used herein interchangeably and intended to mean the same thing; the same is true for the terms spinneret orifice, spinneret aperture, extruder orifice and extruder aperture. The spinneret 14 can generally be heated to a temperature that can allow for the extrusion of the molten polymer while preventing breakage of the filaments 9 during formation. For example, in one embodiment, the spinneret 14 can be heated to a temperature of between about 175°C and about 325°C. In one embodiment, the spinneret 14 can be heated to the same temperature as the mixing manifold 11. This is not a requirement of the process, however, and in other embodiments, the spinneret 14 can be at a different temperature than the mixing manifold 11.

[0034] The spinneret orifices through which the polymer can be extruded can generally be less than about 0.1 inches in maximum cross-sectional distance (e.g., diameter in the particular case of a circular orifice). For example, in one embodiment, the spinneret orifices can be between about 0.002 inches and about 0.050 inches in maximum cross-sectional distance.

[0035] According to the present invention, the polymer can be extruded through the spinneret at a relatively high throughput. For example, the polymer can be extruded through the spinneret at a throughput of not less than about 50% of that required to give melt fracture. In other words, the throughput can be at least 50% of the throughput at which the molten exudate can become excessively distorted. The specific melt fracture throughput can generally vary depending upon one or more of the exudate material, the total number of apertures in the spinneret, the spinneret aperture size, as well as the exudate temperature. For example, when considering the extrusion of molten polypropylene through a spinneret of 8 round apertures of

0.012-inch diameter each, melt fracture can occur at a pump speed of between about 22 and about 24 revolutions/minute of a $0.160 \text{ cm}^3/\text{rev}$ melt pump, or a throughput of about 5.5-6.0 g/min, when extruding a 4 melt flow homopolymer polypropylene at a spinneret temperature of about 230°C . Specific melt fracture throughput values for any particular system and materials as well as methods of obtaining such are generally known to those of skill in the art, and thus a detailed discussion of this phenomenon is not included herein.

[0036] In addition to a relatively high throughput, the filaments can also be formed at a relatively low spinline tension. The combination of high throughput with low spinline tension can allow the filaments to be formed with a relatively low ratio of orifice size to final drawn filament size as compared to other previously known multifilament formation processes. For instance, the ratio of the maximum cross-sectional width of an orifice to the maximum cross-sectional distance of a single fully drawn filament extruded through the orifice can, in one embodiment, be between about 2 and about 10. In one embodiment, this ratio can be between about 3 and about 8. Accordingly, the material forming each filament can be in a fairly relaxed, disorganized state as it begins to cool and crystallize.

[0037] Referring again to Figure 1, following extrusion of the polymer, the undrawn filaments 9 can be quenched in a liquid bath 16 and collected by a take-up roll 18 to form a multifilament fiber structure or fiber bundle 28. While not wishing to be bound by any particular theory, it is believed that by extruding the filaments at a relatively low spinline tension and high throughput combined with quenching the polymeric filaments in a liquid bath, the presently disclosed process encourages the formation of folded chain crystals in a highly disordered state in the polymer, which in turn enables a high draw ratio to be utilized in the process and thereby enables the formation of a multifilament yarn having high tenacity and modulus.

[0038] As is generally known in the art, polymers that are crystallized from a melt under dynamic temperature and stress conditions crystallize with the rate of crystallization dependent upon both the number of nucleation sites as well as on the growth rate of the polymer. Moreover, both of these factors are in turn related to the conditions that the polymer is subject to as it is quenched. In addition, polymers that

crystallize when in a highly oriented state tend to have limited tenacity and modulus as evidenced by the limited draw ratios possible for such highly oriented polymers. Thus, in order to obtain a multifilament yarn with high tenacity and modulus, i.e., formed with a high draw ratio, crystallization of the polymer while in a highly disordered state is suggested. Accordingly, the present invention discloses a multifilament yarn formation process in which crystallization of the polymer in a highly disordered state is promoted by encouraging the filament to maximize its relaxation into the desired disoriented state during crystallization by forming the polymer at a relatively high throughput and low spinline tension. Optionally, a higher rate of crystallization can also be encouraged in certain embodiments through addition of a nucleating agent to the melt. In addition, quenching the formed polymer filaments in a liquid bath can promote the formation of folded chain crystals, which is also associated with the high draw ratios of high tenacity, high modulus materials.

[0039] As described, the individual filaments 9 can be extruded according to the disclosed process at relatively low spinline tension. As such, the take-up roll 18 can operate at a relatively low speed. For example, the take-up roll 18 can generally be set at a speed of less than about 25 meters per minute (m/min). In one embodiment, the take-up roll 18 can be set at a speed of between about 1 m/min and about 20 m/min.

[0040] The liquid bath 16 in which the filaments 9 can be quenched can be a liquid in which the polymer is insoluble. For example, the liquid can be water, ethylene glycol, or any other suitable liquid as is generally known in the art. In one embodiment, in order to further encourage the formation of folded chain crystals in the filaments 9, the bath 16 can be heated. For example, the bath can be heated to a temperature near the maximum crystallization temperature (T_c) of the polymer. For example, the bath can be heated to a temperature of between about 50°C and about 130°C.

[0041] Generally, in order to encourage formation of filaments with substantially constant cross-sectional dimensions along the filament length, excessive agitation of the bath 16 can be avoided during the process.

[0042] In one embodiment, quenching of the polymer can begin as soon as

possible following exit from the spinneret, in order to encourage crystallization of the polymer while in the highly disoriented, relaxed state immediately following extrusion. For example, in one embodiment, the surface of the bath 16 can be located at a minimum distance from the spinneret 14. For instance, in the embodiment illustrated in Figure 2, the surface of the bath 16 can be at a distance from the spinneret 14 such that an extruded filament 9 can enter the bath 16 within the distance of the die swell 31 of the filament 9. Optionally, the individual filaments 9 can pass through a heated or a non-heated shroud prior to entering the bath 16. For example, a heated shroud may be utilized in those embodiments where the distance between the orifice and the bath surface is greater than the die swell. In one embodiment, the distance between the spinneret and the bath can be less than 2 inches. In another embodiment, this distance can be less than 1 inch.

[0043] Take-up roll 18 and roll 20 can be within bath 16 and convey individual filaments 9 and fiber bundle 28 through the bath 16. Dwell time of the material in the bath 16 can vary, depending upon particular materials included in the polymeric material, particular line speed, etc. In general, filaments 9 and subsequently formed fiber bundle 28 can be conveyed through bath 16 with a dwell time long enough so as to ensure complete quench, i.e., crystallization, of the polymeric material. For example, in one embodiment, the dwell time of the material in the bath 16 can be between about 6 seconds and about 1 minute.

[0044] At or near the location where the fiber bundle 28 exits the bath 16, excess liquid can be removed from the fiber bundle 28. This step can generally be accomplished according to any process known in the art. For example, in the embodiment illustrated in Figure 1, the fiber bundle 28 can pass through a series of nip rolls 23, 24, 25, 26 to remove excess liquid from the fiber bundle. Other methods can be alternatively utilized, however. For example, in other embodiments, excess liquid can be removed from the fiber bundle 28 through utilization of a vacuum, a press process utilizing a squeegee, one or more air knives, and the like.

[0045] In one embodiment, a lubricant can be applied to the fiber bundle 28. For example, a spin finish can be applied at a spin finish applicator chest 22, as is generally known in the art. In general, a lubricant can be applied to the fiber bundle

28 at a low water content. For example, a lubricant can be applied to the fiber bundle 28 when the fiber bundle is at a water content of less than about 75% by weight. Any suitable lubricant can be applied to the fiber bundle 28. For example, a suitable oil-based finish can be applied to the fiber bundle 28, such as Lurol PP-912, available from Ghouliston Technologies, Inc. Addition of a finishing or lubricant coat on the yarn can, in some embodiments of the invention, improve handling of the fiber bundle during subsequent processing and can also reduce friction and static electricity build-up on the yarn. In addition, a finish coat on the yarn can improve slip between individual filaments of the yarn during a subsequent drawing process and can increase the attainable draw ratio, and thus increase the modulus and tenacity of the drawn multifilament yarn formed according to the disclosed process.

[0046] After quenching of the fiber bundle 28 and any optional process steps, such as addition of a lubricant for example, the fiber bundle can be drawn while applying heat. For example, in the embodiment illustrated in Figure 1, the fiber bundle 28 can be drawn in an oven 43 heated to a temperature of between about 80°C and about 170°C. Additionally, in this embodiment, the draw rolls 32, 34 can be either interior or exterior to the oven 43, as is generally known in the art. In another embodiment, rather than utilizing an oven as the heat source, the draw rolls 32, 34 can be heated so as to draw the yarn while it is heated. For example, the draw rolls can be heated to a temperature of between about 80°C and about 170°C. In another embodiment, the yarn can be drawn over a hotplate heated to a similar temperature (i.e., between about 80°C and about 170°C). In one embodiment, the oven, draw rolls, hotplate, or any other suitable source of heat can be heated to a temperature of between about 120°C and about 150°C.

[0047] According to the disclosed process, the multifilament fiber bundle can be drawn in a first (or only) draw at a high draw ratio, higher than those attainable in previously known polyolefin melt-spun multifilament yarn formation processes. For example, the fiber bundle 28 can be drawn with a draw ratio (defined as the ratio of the speed of the second or final draw roll 34 to the first draw roll 32) of greater than about 6. For instance, in one embodiment, the draw ratio of the first (or only) draw can be between about 6 and about 25. In another embodiment, the draw ratio can be

greater than about 10, for instance, greater than about 15. Additionally, the yarn can be wrapped on the rolls 32, 34 as is generally known in the art. For example, in one embodiment, between about 5 and about 15 wraps of the yarn can be wrapped on the draw rolls.

[0048] While the illustrated embodiment utilizes a series of draw rolls for purposes of drawing the yarn, it should be understood that any suitable process that can place a force on the yarn so as to elongate the yarn following the quenching step can optionally be utilized. For example, any mechanical apparatus including nip rolls, godet rolls, steam cans, air, steam, or other gaseous jets can optionally be utilized to draw the yarn.

[0049] According to the embodiment illustrated in Figure 1, following the yarn drawing step, the multifilament yarn 30 can be cooled and wound on a take-up roll 40. In other embodiments, however, additional processing of the yarn 30 may be carried out. For example, in one embodiment, the multifilament yarn can be subjected to a second draw. In general, a second drawing step can be carried out at a higher temperature than the first draw. For instance, the heating element of the second drawing step can be heated to a temperature between about 10°C and about 50°C higher than the heating element of the first drawing step. In addition, a second draw can generally be at a lower drawing ratio than the first draw. For example, a second draw can be carried out at a draw ratio of less than 5. In one embodiment, a second draw can be carried out at a draw ratio of less than 3. In the case of multiple draws, the total draw ratio will be the product of each of the individual draws, thus a yarn first drawn at a draw ratio of 3, and then subsequently drawn at a draw ratio of 2 will have been subjected to a total draw ratio of 6.

[0050] Optionally, the drawn multifilament yarn can be heat set. For example, the multifilament yarn can be relaxed or subjected to a very low draw ratio (e.g., a draw ratio of between about 0.7 and about 1.3) and subjected to a temperature of between about 130°C and about 150°C for a short period of time, generally less than 3 minutes. In some embodiment, a heat setting step can be less than one minute, for example, about 0.5 seconds. This temperature can generally be higher than the drawing temperature(s). This optional heat set step can serve to "lock" in the

crystalline structure of the yarn following drawing. In addition, it can reduce heat shrinkage, which may be desired in some embodiments.

[0051] In another embodiment, the finished yarn can be surface treated to improve certain characteristics of the yarn, such as wettability or adhesion, for example. For instance, the yarn can be fibrillated, subjected to plasma or corona treatments, or can include an added surface yarn sizing, all of which are generally known in the art, to improve physical characteristics of the yarns. Beneficially, the multifilament yarns of the invention can have a high surface area available for surface treatments, and thus can exhibit greatly improved characteristics, such as adhesion, as compared to, for instance, monofilament fibers formed of similar materials.

[0052] In general, the finished multifilament yarn 30 can be wound on a spool or take-up reel 40, as shown, and transported to a second location for formation of a secondary product. In an alternative embodiment, however, the multifilament yarn can be fed to a second processing line, where the yarn can be further processed to form a secondary product, such as a woven fabric, for example.

[0053] The polyolefin multifilament yarn of the present invention can generally have a drawn size of between about 0.5 denier per filament and about 100 denier per filament. Beneficially, the disclosed multifilament yarn can have a high tenacity and modulus, as measured in ASTM D2256-02, which is incorporated herein by reference, and as compared to other, previously known multifilament polyolefin yarn. For example, the disclosed multifilament yarn can have a tenacity greater than about 5 grams/denier. In one embodiment, the multifilament yarn can have a tenacity greater than about 7 grams/denier. In addition, the multifilament yarn of the present invention can have a high modulus, for example, greater than about 100 grams/denier. In one embodiment, the disclosed yarn can have a modulus greater than about 125 grams/denier, for example, greater than about 150 grams/denier, or greater than about 200 grams/denier.

[0054] In addition, the disclosed yarn can exhibit relatively low elongation characteristics. For example, the multifilament yarn of the present invention can exhibit an elongation percentage of less than about 15%, as measured in ASTM D2256-02. In another embodiment, the yarn can exhibit less than about 10%

elongation, for example, less than about 8% elongation.

[0055] The inventive multifilament yarns are also believed to possess a unique crystalline structure as compared to other, previously known polyolefin multifilament yarns. There are several widely accepted means by which to measure molecular orientation in oriented polymer systems, among them scattering of light or X-rays, absorbance measurements, mechanical property analysis, and the like. Quantitative methods include wide angle X-ray scattering (WAXS), and small angle X-ray scattering (SAXS).

[0056] Through the utilization of WAXS and SAXS techniques, the disclosed multifilament yarns can be shown to be highly crystalline, highly oriented, with little or no lamellar structure. In particular, the filaments of the yarns can possess greater than about 80% crystallinity according to WAXS measuring techniques described below. For example, Figure 3 illustrates the WAXS scattering pattern of a single filament pulled from a multifilament yarn formed according to the presently disclosed process. In particular, the yarn (listed as sample Q in the Example section, below) was extruded through a spinneret with eight orifices of 0.012 inches diameter each, quenched in a water bath at 73°C, and drawn at a draw ratio of 16.2. The drawn yarn had a final denier of 406 grams/9000 m. As can be seen with reference to the Figure, where 0ϕ is parallel to the yarn, the amorphous region of the disclosed yarns can be 2θ from 10 to 30 and ϕ from 60 to 90 (the dark region near bottom of Figure 3), and the crystalline region can be 2θ from 10 to 30 and ϕ from -15 to 15 (including bright spots on the sides of Figure 3). Thus by integrating the x-ray scattering intensity in the crystalline and amorphous regions, the crystallinity of the filament can be obtained as

$$\frac{(I_X - I_A)}{(I_X)}$$

where: I_X is the intensity in the crystalline region and
 I_A is the intensity in the amorphous region.

[0057] In addition, the polyolefin yarns of the invention can be highly oriented, as shown by the narrow width of the WAXS peaks in Figure 3.

[0058] Figure 4 is the SAXS pattern of the filament shown in Figure 3. Surprisingly, none of the expected structures relating to the crystalline form,

orientation, and amorphous regions appear in the Figure, and the yarn appears to have no true amorphous regions at all, but appears to be composed entirely of crystalline regions and highly oriented amorphous regions.

[0059] SAXS patterns of multifilament yarns formed according to previously known methods generally include alternating crystalline and amorphous regions as illustrated by bright spots of scattering intensity in the yarn axis. (See, for example, Polypropylene Fibers – Science and Technology, M. Ahmed, Elsevier Scientific Publishing Company, 1982, pp. 192-203, which is incorporated herein by reference.) The positions of these spots can be utilized to obtain the long period spacing between repeating crystalline regions. The absence of these spots in Figure 4 indicates that any amorphous regions in the inventive yarn of Figure 4 have nearly identical electron density to the crystalline regions, and are thus composed of dense, highly oriented amorphous chains, or are absent altogether. When combined with the WAXS pattern of Figure 3, which indicates that the amorphous intensity is at least 15%, it may be assumed that amorphous regions of the illustrated filament most likely consists of the highly oriented chains.

[0060] In addition, the equatorial scattering in SAXS patterns in general arises from the center normal to the fiber axis and projects in a long, thin streak away from the center in each direction. In the inventive yarns, and in further reference to Figure 4, these equatorial scattering streaks have amplified greatly, to the point that they are more aptly described as “wings.” This equatorial scattering arises from fibrillation of the crystalline segments into more clearly defined needle-like assemblies. A long equatorial streak arises from a high concentration of cylindrical, shish-type structures in the yarn with the lamellae organized among or around the shishes, as “kabobs.” These streaks generally appear in higher draw situations such as those of the present invention.

[0061] As can also be seen in Figure 4, the filaments forming the yarns of the present invention under high draw conditions can describe a nearly absent meridional reflection and an equatorial scattering that is strong such that the scattering ratio of equatorial to meridional scattering intensity is high, but there remains strong density contrast as indicated by the overall intensity.

[0062] In general, the filaments forming the multifilament yarns of the present invention can have SAXS characteristics including a ratio of equatorial intensity to meridional intensity of greater than about 1.0. In one embodiment, this ratio can be greater than about 3. The filaments forming the disclosed yarns can generally exhibit an equatorial intensity integrated from 2θ of between about 0.4 to about 1.0 and ϕ from about 60 to about 120 and from about 240 to about 300 (zero ϕ being parallel to the yarn, or vertical in reference to Figure 4). In addition, the yarns can exhibit a meridional intensity integrated from 2θ of between about 0.4 and about 1.0 and ϕ from about -60 to about 60 and from about 120 to about 240.

[0063] The disclosed multifilament polyolefin yarns can be beneficially utilized in many applications. For example, the high strength and high tenacity of the disclosed yarns can provide them with excellent qualities for utilization in any application suitable for previously known multifilament polyolefin yarns. For example, in certain embodiments, the disclosed yarns can be beneficially utilized as reinforcement material in a matrix. For example, in one embodiment, following formation of the multifilament drawn yarn according to the disclosed processes, the yarn can be further processed so as to be suitable for use as a reinforcement material in a matrix. For instance, the multifilament yarns of the present invention can be chopped, fibrillated, flattened or otherwise deformed as is generally known in the art. As the multifilament yarns are processed in order to form the disclosed reinforcement materials, the multifilament yarns can not only be shortened, deformed, abraded, and the like, but in addition, the multifilament yarns can become shredded. That is, during processing, individual filaments of the yarns can become separated from one another in forming the disclosed reinforcement materials.

[0064] Accordingly, in one embodiment, the present invention is directed to reinforcement materials formed of the disclosed yarns. In particular, the reinforcement materials of the present invention can include chopped, shredded, and/or degraded yarns as herein described. In general, the reinforcement materials can include relatively short lengths of the multifilament yarns and/or individual filaments that have been shredded off of the formed multifilament yarns. For example, the reinforcement materials of the present invention can generally be less

than about 5 inches in length. In one embodiment, the reinforcement materials can be less than about 3 inches in length, for instance, less than about 1 inch in length,

[0065] During use, the reinforcement materials of the disclosed invention can be combined with a matrix material such as adhesives, asphalt, plastics, rubber, or hydratable cementitious compositions including ready-mix or pre-cast concrete, masonry concrete, shotcrete, bituminous concrete, gypsum compositions, cement-based fireproofing compositions, and the like.

[0066] In one embodiment of the present invention, the disclosed yarns can be further processed if necessary and utilized in forming secondary products including those products that in the past have been formed with previously known multifilament polyolefin yarns. For example, the disclosed yarns can be utilized in forming ropes, and woven or nonwoven fabrics such as may be found in machinery belts or hoses, roofing fabrics, geotextiles, and the like. In particular, the disclosed multifilament yarns can be suitable for use in forming a secondary product according to any known technique that has been used in the past with previously known polyolefin multifilament yarns. Due to the improved physical properties of the disclosed yarns, however, and particularly, the higher modulus and tenacity of the disclosed yarns, secondary products formed utilizing the inventive yarns can provide improved characteristics, such as strength and tenacity, as compared to similar products formed of previously known multifilament polyolefin yarns.

The invention may be better understood with reference to the following Example.

Example

[0067] Yarn samples were formed on system similar to that illustrated in Figure 1. In particular, the system included a $\frac{3}{4}$ inch, 24:1 single screw extruder with three temperature zones, a head with a melt pump and spinneret, a liquid quench tank (40 inch length), with two rollers in the tank, a vacuum water removal system, a spin finish applicator, three heated godet rolls, a forced air oven (120 inch length) and a Leesona® winder.

[0068] Materials utilized in forming the yarns included Atofina® 3462, a polypropylene homopolymer with a melt flow index of 3.7 and Atofina® 3281, a

polypropylene homopolymer with a melt flow index of 1.3 (both available from ATOFINA Petrochemicals, Inc. of Houston, TX), a 10% concentrate of a nucleating agent composition, specifically Millad® 3988 (3,4-dimethyl dibenzylidene sorbitol) in a 12 MFI polypropylene homopolymer (available from Standridge Color Corporation, Social Circle, GA, USA), and a polyethylene homopolymer with a melt flow index of 12 (available from TDL Plastics, of Houston, TX).

[0069] Table 1, below, tabulates the formation conditions of 37 different samples including the material make-up (including the polymer used and the total weight percent of the nucleating agent in the melt), the spinneret hole size in inches, the total number of filaments extruded, the temperature of the quench water bath, the roll speeds of the drawing rolls, the total draw ratio (Roll 3/Roll 1), and the temperature of the drawing oven. In addition, as the nucleating agent is provided in a 10% concentrate composition of the nucleating agent in a 12 MFI polypropylene homopolymer, the material make-up of those samples that include an amount of a nucleating agent will also include an amount of the 12 MFI polypropylene homopolymer from the concentrate. For example, a sample that is listed as containing FINA 3462/0.2% Millad will contain 0.2 wt% of the nucleating agent, 1.8 wt% of the 12 MFI polypropylene homopolymer used in forming the 10% nucleating agent composition, and 98 wt% of the FINA 3462 3.7 MFI polypropylene homopolymer.

Table 1

Sample	Material	Spinneret Hole Size	# Fils	Water Temp	Roll 1	Roll 2	Roll 3	DR	Oven T
		inches	#	C	m/min	m/min	m/min		°C
A	Fina 3462	0.04	1	25	11.3	100	110	9.7	120
B	Fina 3462/0.2% Millad	0.04	1	25	8	123	123	15.4	140
C	Fina 3462/0.2% Millad	0.027	17	25	5	30	30	6.0	120
D	Fina 3462/0.2% Millad	0.027	17	25	5	37.5	37.5	7.5	150
E	Fina 3462/0.25% Millad	0.018	1	25	10.5	135	135	12.9	130
F	Fina 3462/0.25% Millad	0.018	8	25	9	85	85	9.4	130
G	Fina 3462/0.25% Millad	0.018	8	25	6	85	85	14.2	130
H	Fina 3462/0.25% Millad	0.012	8	25	8.75	85	85	9.7	130
I	Fina 3462/0.25% Millad	0.012	8	25	9.5	85	85	8.9	130
J	Fina 3462/0.20% Millad	0.012	8	25	8	85	85	10.6	130
K	Fina 3462/0.20% Millad	0.012	8	25	6.25	85	85	13.6	130
L	Fina 3462/0.20% Millad	0.012	8	25	5.5	85	85	15.5	130
M	Fina 3462/0.20% Millad	0.012	8	25	5.5	85	85	15.5	130

N	Fina 3462/0.20% Millad	0.012	5	25	5	85	85	17.0	130
O	Fina 3462/0.20% Millad	0.012	5	55	6	85	85	14.2	130
P	Fina 3462/0.20% Millad	0.012	5	55	6	85	85	14.2	130
Q	Fina 3462/0.20% Millad	0.012	8	73	5.25	84	85	16.2	130
R	Fina 3462/0.20% Millad	0.012	8	85	5.5	84	85	15.5	130
S	Fina 3462/0.20% Millad	0.012	8	85	5.25	84	85	16.2	130
T	Fina 3462/0.20% Millad	0.012	8	82	4.75	84	85	17.9	145
U	Fina 3462/0.20% Millad	0.012	8	82	4.6	84	85	18.5	150
V	Fina 3281/ 0.2% Millad	0.012	8	75	4.5	84	85	18.9	140
W	Fina 3281/ 0.2% Millad	0.012	8	75	4.5	84	85	18.9	140
X	Fina 3281	0.012	8	75	6	84	85	14.2	130
Y	Fina 3281	0.012	8	75	4.5	84	85	18.9	140
Z	Fina 3281	0.012	8	75	4.25	84	85	20.0	140
AA	Fina 3281w/ 5% 12 MFI PE	0.012	8	75	5	84	85	17.0	130
BB	Fina 3281/0.2% Millad	0.012	8	75	4.75	84	85	17.9	150
CC	Fina 3281/0.2% Millad	0.012	8	75	4.25	84	85	20.0	140
DD	Fina 3281/0.2% Millad	0.012	8	75	4	84	85	21.3	140
EE	Fina 3281/0.2% Millad	0.012	8	75	4	84	85	21.3	140
FF	Fina 3281/0.2% Millad	0.012	8	75	4	84	85	21.3	140
GG	Fina 3281/0.2% Millad	0.012	8	75	5	84	85	17.0	140
HH	Fina 3281/0.2% Millad	0.012	8	75	4.75	84	85	17.9	140
II	Fina 3281/0.2% Millad	0.008	20	75	4.25	84	85	20.0	140
JJ	Fina 3281/0.2% Millad	0.008	20	75	5.5	84	85	15.5	150
KK	Fina 3281/0.2% Millad	0.008	20	75	4.25	84	85	20.0	140

[0070] Following formation, the samples were tested for a number of physical properties including denier, denier per filament, elongation, tenacity, modulus, and toughness, all according to ASTM D2256-02, previously incorporated by reference. Results are shown below in Table 2.

Table 2

Sample	Material	Denier	Den/fil	Elong	Ten	Mod	Tuff
		g/9000 m	g/9000 m	%	g/d	g/d	g/d
A	Fina 3462	302	302	24	5.2	60	
B	Fina 3462/0.2% Millad	292	292	8	5.9	107	
C	Fina 3462/0.2% Millad	1300	76	21	5.5	50	
D	Fina 3462/0.2% Millad	1414	83	16	4.2	43	
E	Fina 3462/0.25% Millad	63	63	10	7.9	125	
F	Fina 3462/0.25% Millad	293	37	22	8.5		
G	Fina 3462/0.25% Millad	532	67	11.7	10.4	173	
H	Fina 3462/0.25% Millad	210	26	16.9	8.1	100	
I	Fina 3462/0.25% Millad	161	20	14.8	7.2	100	
J	Fina 3462/0.20% Millad	222	28	15.0	9.0	108	
K	Fina 3462/0.20% Millad	316	40	9.1	8.4	154	

L	Fina 3462/0.20% Millad	362	45	8.9	8.8	159	
M	Fina 3462/0.20% Millad	420	53	11.2	9.6	146	
N	Fina 3462/0.20% Millad	297	59	10.4	10.5	171	
O	Fina 3462/0.20% Millad	287	57	11.3	9.4	144	
P	Fina 3462/0.20% Millad	276	55	9.2	7.7	132	
Q	Fina 3462/0.20% Millad	406	51	9.3	11.6	207	
R	Fina 3462/0.20% Millad	369	46	14.0	8.2		
S	Fina 3462/0.20% Millad	390	49	14.0	8.4		
T	Fina 3462/0.20% Millad	345	43	9.3	10.4	189	
U	Fina 3462/0.20% Millad	324	41	8.8	10.9	201	
V	Fina 3281/ 0.2% Millad	353	44	7.3	9.3	185	
W	Fina 3281/ 0.2% Millad	358	45	6.9	9.7	203	
X	Fina 3281	329	41	12.5	9.3	131	0.75
Y	Fina 3281	301	38	10.7	10.3	160	0.73
Z	Fina 3281	316	40	9.7	9.8	165	0.66
AA	Fina 3281w/ 5% 12 MFI PE	328	41	14.0	8.9		
BB	Fina 3281/0.2% Millad	270	34	9.1	8.5	159	0.62
CC	Fina 3281/0.2% Millad	287	36	8.6	8.9	181	0.58
DD	Fina 3281/0.2% Millad	265	33	8.9	10.4	203	0.68
EE	Fina 3281/0.2% Millad	364	46	8.1	9.1	178	0.61
FF	Fina 3281/0.2% Millad	403	50	6.5	8.5	181	0.41
GG	Fina 3281/0.2% Millad	356	45	8.4	10.3	200	0.60
HH	Fina 3281/0.2% Millad	375	47	5.3	8.8	203	0.39
II	Fina 3281/0.2% Millad	396	20	6.4	8.3	178	0.46
JJ	Fina 3281/0.2% Millad	589	29	9.6	9.2	166	0.65
KK	Fina 3281/0.2% Millad	423	21	6.1	7.8	178	0.47

X-ray Scattering Analysis

[0071] The samples were studied by small angle x-ray scattering (SAXS). The SAXS data were collected on a Bruker AXS (Madison, Wis.) Hi-Star multi-wire detector placed at a distance of 105.45 cm from the sample in an Anton-Paar vacuum. X-rays ($\lambda=0.154178$ nm) were generated with a MacScience rotating anode (40 kV, 40 mA) and focused through three pinholes to a size of 0.2 mm. The entire system (generator, detector, beampath, sample holder, and software) is commercially available as a single unit from Bruker AXS. The detector was calibrated per manufacturer recommendation using a sample of silver behenate.

[0072] A typical SAXS data collection was conducted as follows: A polypropylene filament bundle was wrapped around a holder, which was placed in the x-ray beam inside an Anton-Paar vacuum sample chamber on the x-ray equipment. The sample chamber and beam path was evacuated to less than 100 mTorr and the

sample was exposed to the X-ray beam for between about 45 minutes and one hour. Two-dimensional data frames were collected by the detector and unwarped automatically by the system software.

[0073] An analysis of the scattered intensity distribution ($2\theta=0.2^\circ - 2.5^\circ$) into the equatorial or meridional directions was calculated from the raw data frames by dividing the scattering into 2 regions: an equatorial scattering region, integrated from 2θ of between about 0.4 to about 1.0 and ϕ from about 60 to about 120 and from about 240 to about 300 (zero ϕ being parallel to the yarn, or vertical in Figure 4), and the meridional scattering region, integrated from 2θ of between about 0.4 and about 1.0 and ϕ from about -60 to about 60 and from about 120 to about 240. Total counts were summed for each of the two regions and the ratio calculated and tabulated for each sample in Table 3, below.

Table 3

Sample	Material	Meridional Scattering	Equatorial Scattering	Equatorial/ Meridional
		counts	counts	
A	Fina 3462	150499	18174	0.12
B	Fina 3462/0.2% Millad	83716	293818	3.51
C	Fina 3462/0.2% Millad	125348	20722	0.17
D	Fina 3462/0.2% Millad	169657	37642	0.22
E	Fina 3462/0.25% Millad	57067	265606	4.65
F	Fina 3462/0.25% Millad	28192	23494	0.83
G	Fina 3462/0.25% Millad	34164	182207	5.33
H	Fina 3462/0.25% Millad	14203	11505	0.81
I	Fina 3462/0.25% Millad	21722	17758	0.82
J	Fina 3462/0.20% Millad	36264	74971	2.07
K	Fina 3462/0.20% Millad	82734	662846	8.01
L	Fina 3462/0.20% Millad	47815	175599	3.67
M	Fina 3462/0.20% Millad	53247	323136	6.07
N	Fina 3462/0.20% Millad	89254	561719	6.29
O	Fina 3462/0.20% Millad	52212	313477	6.00
P	Fina 3462/0.20% Millad	57344	365467	6.37
Q	Fina 3462/0.20% Millad	107220	401479	3.74
R	Fina 3462/0.20% Millad	40419	59163	1.46
S	Fina 3462/0.20% Millad	48712	106876	2.19
T	Fina 3462/0.20% Millad	49098	153474	3.13
U	Fina 3462/0.20% Millad	65459	210907	3.22
V	Fina 3281/ 0.2% Millad	54222	220056	4.06
W	Fina 3281/ 0.2% Millad	43058	257097	5.97

X	Fina 3281	53060	159811	3.01
Y	Fina 3281	57218	210415	3.68
Z	Fina 3281	45224	186045	4.11
AA	Fina 3281w/ 5% 12 MFI PE	35826	87938	2.45
BB	Fina 3281/0.2% Millad	37907	98972	2.61
CC	Fina 3281/0.2% Millad	54109	164494	3.04
DD	Fina 3281/0.2% Millad	47656	202256	4.24
EE	Fina 3281/0.2% Millad	51026	171581	3.36
FF	Fina 3281/0.2% Millad	48872	181346	3.71
GG	Fina 3281/0.2% Millad	49382	282585	5.72
HH	Fina 3281/0.2% Millad	54467	348671	6.40
II	Fina 3281/0.2% Millad	57703	260487	4.51
JJ	Fina 3281/0.2% Millad	52353	178923	3.42
KK	Fina 3281/0.2% Millad	46881	203281	4.34

[0074] As can be seen with reference to Table 3, while the disclosed materials can in some cases give to rise to a SAXS scattering profile with both meridional scattering and equatorial scattering, the meridional scattering is low compared to the highly unique strong equatorial scattering giving rise to a high ratio of equatorial scattering to meridional scattering. At the very least, then, the presence of intense scattering wings in the equatorial direction provides the desired crystal structures that impart the properties of high tenacity and high modulus found in the multifilament yarns.

[0075] It will be appreciated that the foregoing examples, given for purposes of illustration, are not to be construed as limiting the scope of this invention. Although only a few exemplary embodiments of this invention have been described in detail above, those skilled in the art will readily appreciate that many modifications are possible in the exemplary embodiments without materially departing from the novel teachings and advantages of this invention. Accordingly, all such modifications are intended to be included within the scope of this invention that is defined in the following claims and all equivalents thereto. Further, it is recognized that many embodiments may be conceived that do not achieve all of the advantages of some embodiments, yet the absence of a particular advantage shall not be construed to necessarily mean that such an embodiment is outside the scope of the present invention.

WHAT IS CLAIMED IS:

1. A method comprising:
 - forming a melted polymeric composition comprising at least one polyolefin;
 - extruding the melted polymeric composition through multiple orifices to form multiple filaments of the polymeric composition;
 - quenching the filaments in a liquid bath;
 - collecting the filaments to form a multifilament fiber bundle; and
 - drawing the multifilament fiber bundle with a draw ratio greater than 6 to form a drawn multifilament yarn, wherein the multifilament fiber bundle is drawn while heated, the heat source being at a temperature of between 80°C and 170°C, and wherein at least one of said filaments has a ratio of equatorial intensity to meridional intensity greater than 3.0 according to SAXS measuring techniques.
 2. The method of claim 1, wherein the polymeric composition comprises at least two polyolefins.
 3. The method of claim 1 or 2, wherein the polyolefin is a polypropylene,
 4. The method of claim 3, wherein the polypropylene has a melt flow index of between 0.2 and 50.
 5. The method of any one of the preceding claims, wherein each orifice defines a maximum cross-section of between 0.002 inches and 0.050 inches.
 6. The method of any one of the preceding claims, wherein the filaments are extruded at a rate of between 1 meter per minute and 25 meters per minute.
- The method of any one of the preceding claims, in which the liquid bath is heated.

8. The method of any one of the preceding claims, wherein the extruded filaments each describe a die swell adjacent to the orifice, the surface of the liquid bath being within the distance of the die swell.

9. The method of any one of the preceding claims, wherein the fiber bundle is drawn utilizing an oven or draw rolls heated to a temperature of between 80°C and 170°C.

10. The method of any one of the preceding claims, wherein the draw ratio is between 6 and 25.

11. The method of any one of the preceding claims, wherein the draw ratio is greater than 10.

12. The method of any one of the preceding claims, further comprising drawing the drawn multifilament yarn a second time, wherein the second draw ratio is less than the first draw ratio.

13. The method of any one of the preceding claims, further comprising heat setting the drawn multifilament yarn.

14. The method of any one of the preceding claims, wherein the ratio of the maximum cross-sectional dimension of a single orifice to the maximum cross-sectional dimension of the single drawn filament extruded from that orifice is between 1 and 10.

15. The method of any one of the preceding claims further comprising forming a secondary product comprising the drawn multifilament yarn, the secondary product being selected from the group consisting of a rope, a woven fabric, and a nonwoven fabric

16. A method of forming a multifilament yarn comprising:

forming a melted polymeric composition comprising a polypropylene having a melt flow index of between 2 and 50 ,

extruding the melted polymeric composition through multiple orifices at a rate of between 1 meter per minute and 25 meters per minute to form multiple filaments of the polymeric composition.

quenching the filaments in a heated liquid bath

collecting the quenched filaments to form a multifilament fiber bundle,

applying a lubricant to the fiber bundle and

drawing the multifilament fiber bundle with a draw ratio greater than 6 to form a drawn multifilament yarn, wherein the multifilament fiber bundle is drawn while heated, the heat source being at a temperature of between 80°C and 170°C

17. The method of claim 16 wherein each orifice defines a maximum cross-section of between 0.002 inches and 0.050 inches

18. The method of claim 16 or 17, in which the liquid bath is heated to a temperature of between 50°C and 130°C.

19. The method of any one of claims 16 to 18, wherein the fiber bundle is drawn utilizing an oven or draw rolls heated to a temperature of between 80°C and 170°C

20. The method of any one of claims 16 to 19, wherein the ratio of the maximum cross-sectional dimension of a single orifice to the maximum cross-sectional dimension of the drawn filament extruded from that orifice is between 1 and 10.

21. A drawn multifilament yarn comprising at least three filaments, each filament including a polyolefin and each filament having a denier of less than 300 grams/9000 meters, the drawn multifilament yarn having been drawn at a draw ratio of greater than 6 and the drawn multifilament yarn having a modulus greater than 40 grams/denier wherein at least one of the filaments possesses greater than about 80% crystallinity according to WAXS measuring techniques.

22. The drawn multifilament yarn of claim 21, wherein the yarn has a tenacity greater than 5 grams/denier.

23. The drawn multifilament yarn of claim 21 or 22, wherein each filament has a denier of between 0.5 grams/9000 meters and 100 grams/9000 meters,

24. The drawn multifilament yarn of any one of claims 21 to 23, wherein the polyolefin is a polypropylene.

25. The drawn multifilament yarn of any one of claims 21 to 24, wherein the yarn has a modulus greater than 100 grams/denier.

26. The drawn multifilament yarn of any one of claims 21 to 25, wherein the yarn has a modulus greater than 150 grams/denier,

27. The drawn multifilament yarn of any one of claims 21 to 26, wherein the yarn has a tenacity greater than 7 grams/denier.

28. The drawn multifilament yarn of any one of claims 21 to 27, wherein the yarn exhibits an elongation of less than 10%,

29. The drawn multifilament yarn of any one of claims 21 to 28, wherein at least one of the filaments

has a ratio of equatorial intensity to meridonal intensity greater than 1.0 according to SAXS measuring techniques

30. The drawn multifilament yarn of any one of claims 21 to 29 wherein at least one of the filaments has a ratio of equatorial intensity to meridonal intensity greater than 3.0 according to SAXS measuring techniques

31. The drawn multifilament yarn of claim 29, the yarn further comprising a nucleating agent

32. The drawn multifilament yarn of claim 31 wherein the nucleating agent is a dibenzylidene sorbitol nucleating agent

33. The drawn multifilament yarn of claim 29, wherein the yarn is contained within a secondary product selected from the group consisting of a rope, a woven fabric, and a nonwoven fabric

34. A reinforcement material comprising a yarn of a length of less than five inches, the yarn comprising at least three filaments each filament comprising a polyolefin and exhibiting a denier of less than 300 grams/9000 meters, the yarn having been drawn at a draw ratio of greater than 6 and having a modulus greater than 40 grams/denier, wherein the reinforcement material is for reinforcing a matrix material

35. The reinforcement material of claim 34, wherein the yarn has been degraded

36. The reinforcement material of claim 34 or 35, wherein the yarn has been deformed

37. The reinforcement material of any one of claims 34 to 36, wherein the yarn is less than three inches in length

38. The reinforcement material of any one of claims 34 to 37, wherein the reinforcement material is for reinforcing a hydratable cementitious composition

39. The reinforcement material of any one of claims 34 to 38, wherein the yarn has a tenacity greater than 5 grams/denier

40. The reinforcement material of any one of claims 34 to 39, wherein the polyolefin is a

polypropylene.

41. The reinforcement material of any one of claims 34 to 40, wherein the yarn has a modulus greater than 100 grams/denier.