FIG. 5

POLYMER

SCREW MELTER

ADDITIVE SUPPLY

FEED PUMP

MIXER

METERING PUMP

SPINNERET

WINDUP

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MELT SPINNING PROCESS FOR PRODUCING HOLLOW-CORE FILAMENT
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This invention relates to the manufacture of textile fibers. More particularly, it is concerned with an improved method of preparing hollow fibers from synthetic polymers.

The textile industry has long been interested in hollow fibers because of the special attributes of such fibers and the many novel effects which may be obtained with them. In addition to lower apparent density and lower rate of heat transfer, hollow fibers also exhibit reduced pilling in staple fiber fabrics and show special optical effects such as higher opacity, or sparkle and glitter, depending upon the shape of the fiber cross section. Many processes have been proposed for preparing hollow synthetic fibers. As early as 1924, Rouset (U.S. Patent No. 1,487,807 and U.S. Patent No. 1,464,048) disclosed that hollow cellulose filaments could be prepared from viscose solutions by dissolving air in the spinning solution under pressure and then extruding the solution through conventional spinneret orifices. However, attempts to utilize this method for producing hollow fibers of synthetic polymers by melt-spinning processes have not been successful. Thus Miles disclosed, in U.S. Patent No. 2,268,160, that spongy cellular products useful as leather substitutes were obtained.

Processes which have been proposed previously for melt-spinning synthetic superpolymers directly into hollow textile filaments have involved complicated techniques such as the use of special spinnerset capable of supplying a gas to the center of each filament cross section as it is extruded from the spinneret, or of forming a cluster of small filaments which coalesce immediately below the face of the spinneret into a larger hollow filament. The method which involves positively supplying a gas to the center of the filament suffers from the disadvantage of the high cost of preparing such complicated spinnersets, as well as the difficulty of maintaining such spinnersets in good condition through the frequent cleaning operations which must be performed. The method of preparing hollow filaments by coalescence, on the other hand, suffers from the disadvantage of the frequent occurrence of failure of coalescence at some point, especially when spinning lower viscosity polymer. If, in order to insure coalescence, the holes in each cluster producing a hollow filament are closely spaced so that the individual streams coalesce before leaving the face of the spinneret, then there is no opening for air to enter the hollow cavity and the filament immediately collapses so that no hollow cavity, or only a very small one, is present in the final filament. It is an object of this invention to provide an improved process for melt-spinning synthetic linear polymers directly into hollow filaments. A further object is the provision of such a process for preparing hollow filaments from synthetic polymers in which the size of the filament cavity may be varied without change in the spinneret orifice. Another object is the provision of a procedure for preparing a hollow filament having a uniform longitudinal cavity surrounded by non-cellular sheath polymer. Other objects will become apparent from the following description and claims.

These objects are accomplished by the following invention which provides for the production of hollow textile filaments by a molten synthetic linear fiber-forming polymer containing a minor amount of gaseous or gas-forming material through a center-obstructed orifice to form a filament, and then quenching the extruded filament. Subsequently, the quenched hollow filament may be drawn according to normal drawing procedures if desired.

Surprisingly, the process of this invention does not produce a cellular or spongy polymeric filament, but rather, a uniform continuous hollow filament having a solid polymeric sheath.

In the drawing, which illustrates apparatus for use in the process and the product improvement achieved, FIGURE 1a is a greatly enlarged view of a portion of the face of a spinneret plate, showing one of the spinning orifices, FIGURE 1b is a corresponding cross-sectional view through the spinneret plate, taken along line b—b of FIGURE 1.

FIGURE 2 is a greatly enlarged view of a filament cross section obtained in accordance with this invention when using the spinning orifice of FIGURE 1, FIGURE 3 shows for comparison with FIGURE 2 a filament cross section obtained when no gaseous material is present in the polymer during spinning. FIGURES 4a and 4b are views corresponding to FIGURES 1a and 1b of another form of spinneret orifice, and FIGURE 5 is a diagrammatic flow sheet indicating essential components of one form of apparatus useful in practicing the invention.

The process of this invention is particularly useful for fiber-forming synthetic polymers which are normally melt spun without the addition of a solvent or a plasticizing agent. Polymers suitable for use in this process include, for example, superpolymers such as poly(ethylene terephthalate) and poly(hexahydro-p-xylene terephthalate) and superpolymides such as poly(hexamethylene adipamide) and polyacrylamide. The preparation of such polymers is described in U.S. Patents Nos. 2,071,250, 2,071,253, 2,130,948, 2,465,319, and 2,901,466. Other classes of polymers suitable for use in this invention include the polypeptides, the polyamides, the polyhydroxides, and the polyureas, and other crystalline synthetic linear fiber-forming polymers suitable for being spun. Without limitation, for example, may be added during the formation of the polymer itself, or mixed with polymer flakes before it is melted for the spinning
operation. Useful gas-forming materials of this type include inorganic salts such as zinc carbonate, organic compounds such as oxalic acid, and organic polymers such as the polycarbonates, e.g., the polycarbonate of diphenyl carbonate. It is particularly advantageous to use a material which is soluble in the polymer at the temperature and pressure used, since a homogeneous solution leads to greater uniformity of product as well as fewer spinning interruptions.

Only a minor amount of the gaseous or gas-forming material need be added to the polymer for the process of this invention. Enough gas-forming material should be present to form a volume of gas, at the temperature of extrusion, equal to about 5 to 85% of the volume of the filament. For the preferred low-boiling fluids, the amount required falls in the range of 0.05 to 4.0% by weight, based upon the weight of the polymer. Within this range, the concentration of gaseous fluid may be varied as described to produce a larger or smaller cavity within the hollow filament.

One of the advantages of this invention is the facility with which the size of the void within a hollow filament, spun from a given orifice, may be changed by simply changing the concentration of gaseous material present in the polymer upon extrusion.

The spinneret orifice required for the process of this invention may be of any suitable shape, i.e., circular, triangular, rectangular, or of some irregular shape. The chief requirement is that some portion of the center of the orifice be obstructed. Thus, for a circular orifice, the shape of the opening through which the polymer is extruded will be that of an annular ring. The annular opening at the spinneret face must not be broken at any point, for in order to maintain full control over the size of the void in the hollow filament, it is necessary that the polymer sheath be continuous and unbroken. In its simplest form, the orifice may take the form of a circular hole with a wire inserted through its axis as illustrated in FIGURE 4. Other methods of constructing suitable spinneret orifices will come readily to mind to those skilled in the art, bearing in mind that a major requirement is that the polymer sheath have an unbroken periphery as it leaves the spinneret face.

It is to be understood that the process of this invention is similar to normal melt-spinning procedures in all respects with the exception of the presence of a gaseous or gas-forming material in the polymer at the moment of extrusion and the use of a center-obstructed orifice in the spinneret. Thus, many variations in the process of this invention will be apparent to those skilled in the melt-spinning art.

The following examples illustrate specific embodiments of the invention. In the examples, the term "intrinsic viscosity" refers to the limit of the fraction

$$\ln (r) \over c$$

as $c$ approaches 0, where $r$ is the relative viscosity and $c$ is the concentration in grams per 100 ml of solution. The relative viscosity is the ratio of the viscosity of a solution of the polymer in a suitable solvent to the viscosity of the solvent per se measured in the same units at 25°C. A suitable solvent for polyesters is a mixture of 10 parts of phenol and 7 parts of 2,4,6-trichlorophenol by weight. Intrinsic viscosity is a measure of the degree of polymerization.

**Example I**

Polyethylene terephthalate having an intrinsic viscosity of 0.6 is melt-spun using the equipment shown schematically in FIGURE 5. The temperature of the screw molder is 290°C, the temperature of the spinneret is 296°C, and the metering pump is set to deliver a polymer flow of 49.5 grams per minute to the spinning head. The spinneret used has 34 holes of the type shown in FIGURE 1a with the length of each side of the outer triangle being 0.035 inch, and the slit width being 0.003 inch. The capillary length of the hole is 0.012 inch. The feeder pump shown in FIGURE 5 is supplied with the halocarbon CCl₃FCCl₂F and set to deliver 1.2 grams per minute to the polymer stream. The halocarbon is thoroughly mixed with the molten polymer by means of the transfer line mixer shown in FIGURE 5. The extruded filaments are quenched in air and wound up at a speed of 1600 yards per minute. Subsequently, the filaments are heated to a temperature of 95°C and drawn over a pin using a draw ratio of 2.3x giving a 34 filament yard having a denier of 132 (15 Tex)., a tenacity of 3 g.p.d., and a break elongation of 30%. The resulting smooth, uniform filaments, when examined under a microscope, are found to have a cross section similar to that shown in FIGURE 2. The void content of the filament cross section is found to be approximately 40%. The percent void content is defined as

$$\left( {\text{I.D.}} \over {\text{O.D.}} \right)^2 \times 100$$

where I.D. equals inside diameter and O.D. equals outside diameter.

The experiment is repeated with no halocarbon fed into the polymer stream. The resulting filament, examined under a microscope, has a cross section of the type shown in FIGURE 3. The void content is found to be approximately 1.5%.

**Example II**

The experiment of Example I is repeated using a rate of feed of halocarbon double that of Example I, i.e., about 2.4 grams per minute. The filaments produced are essentially round in cross section and have a void content of approximately 70%.

**Example III**

The experiment of Example I is repeated using a high boiling organopolysiloxane fluid having a viscosity of 500 centistokes at 25°C. (Dow Corning 710 Silicone Fluid) instead of the halocarbon. The polysiloxane fluid is added to the molten polymer at a rate of about 0.49 gram per minute, giving a concentration of 1% based upon the weight of the polymer. The filaments produced are found to have a cross section similar to that of FIGURE 2.

**Example IV**

The experiment of FIGURE 1 is repeated using polyhexamethylene adipamide flake having an intrinsic viscosity of 0.95 instead of polyethylene terephthalate. The halocarbon is fed in at a rate of 1.5 grams per minute. The filaments are drawn at room temperature. The resulting fibers are smooth, uniform, and continuous, and are found to be hollow with a cross section similar to that of FIGURE 2.

When the experiment is repeated without the addition of the halocarbon, the fibers have a cross section similar to that of FIGURE 3.

**Example V**

100 parts of polyethylene terephthalate flake of 0.6 intrinsic viscosity are tumbled with 2.4 parts of CCl₃FCCl₂F for 60 minutes in a closed container. The flake is then fed into the screw meter of FIGURE 5 and melt-spun as in Example I with the exception that no additional halocarbon is added to the molten polymer by means of the pump. The filaments are drawn as in Example I and the cross sections examined under a microscope. The cross sections are found to be similar to that of FIGURE 2.

The experiment is repeated using a spinneret having orifices similar to that shown in FIGURE 4. The resulting filaments have a round cross section with a void content of 10-15%.
Example VI

An 80/20 copolymer of polyethylene terephthalate/polyethylene isophthalate having an intrinsic viscosity of 0.60 is fed to the screw melt of FIGURE 5 and melt spun using a meter temperature of 290 °C. and a spinneret temperature of 290 °C. In place of the feeder pump shown in FIGURE 5, the polymer transfer line is connected to a nitrogen supply line through which nitrogen gas is metered to the polymer by means of a needle valve, a pressure gage, and a flow meter. Nitrogen gas is supplied at a rate of 20 cubic centimeters per minute. The polymer is extruded at the rate of 49.5 grams per minute. The drawn filaments are found to have a tenacity of 3.5 grams per denier, a break elongation of 25%, and filament cross section similar to that of FIGURE 2. The void content of the filament is approximately 25%.

Example VII

Finely-divided polyethylene terephthalate flake of intrinsic viscosity 0.66 is tumbled with powdered poly(diphenylolpropone carbonate) having an intrinsic viscosity of 0.76. The polycarbonate is present in an amount equivalent to 1% by weight of the total weight of the polymer mixture. The polymer mixture is melted in a screw extruder, transported in molten condition to a standard melt spinning apparatus, and melt spun at a temperature of 305 °C. Through a spinneret having 34-center-obstructed orifices of a type similar to FIGURE 1. The extruded filaments are wound up at 1600 y.p.m. and drawn according to known methods to give 34 filament yarn having a total denier of 150 (17 Tex.). The yarn is found to have a tenacity of 3.8 g.p.d., a break elongation of 34%, an initial modulus of 34 g.p.d., and a boil-off shrinkage of 0.0%. Each individual filament for intrinsic viscosity 0.66 is found to have a continuous longitudinal void surrounded by a solid polymer sheath, with the void content being approximately 24%.

Example VIII

The experiment of Example VII is repeated using polyl(diphenylolpropone carbonate) at concentration levels of 0.1% and 5.0%. The filaments produced with the lower content of polycarbonate are found to have a void content of about 6%. Filaments produced with the higher concentration of polycarbonate are found to have a void content of about 70%.

Example IX

Finely-divided polyethylene terephthalate flake having an intrinsic viscosity of 0.64 is tumbled with powdered zinc carbonate at concentrations of 0.25 and 0.12% by weight. The two mixtures are melt-spun at 298 °C and subsequently drawn to give 34-filament yarns having deniers of approximately 150 (17 Tex.). Examination of the filaments under a microscope shows that the filaments consist of a continuous uniform longitudinal void surrounded by a solid polymer sheath. The void content for the higher concentration of zinc carbonate is about 18%, while that for the lower concentration of zinc carbonate is about 8%.

Example X

The procedure of Example VII is repeated with the exception that the poly(diphenylolpropone carbonate) is replaced with finely-divided poly(diethylenehexyladipyl chloride) having an intrinsic viscosity of 0.56, and spinning is carried out at 296 °C. Upon microscopic examination the yarn produced is found to have a continuous longitudinal void surrounded by a solid polymer sheath, with the void content being 12-15%. It is noted that the color of the yarn is at least as good as that spun from polyethylene terephthalate without an additive.

Although the preceding examples have illustrated this invention in terms of certain specific polyesters and polyamides, it is to be understood that any other synthetic fiber-forming linear superpolymer capable of being melt spun may be substituted in the examples with equivalent results. Among other polymers suitable for use in this process of this invention, the following polymers may be mentioned: polyethylene, polypropylene; poly(ethylene-2,6-naphthalate); poly(m-xylene adipamide); polyvinyl chloride; polyvinylidene chloride; the polynaphthenes from 1,4-butanediol and hexamethylenedichloride; the polyester from ethylene glycol, terephthalic acid and benzene acid; the polyamide from bis(p-aminocyclohexyl)-methane and azelaic acid; the block copolymer from poly(hexamethylene adipamide) and poly(hexamethylene isophthalamide); the copolyester from ethylene glycol, terephthalic acid, and isophthalic acid; and poly(tetra-chlorodiethyleneolpropone isophthalate) to name a few. Even glass may be used with proper choice of conditions.

The fibers prepared by the process of this invention may contain various modifying agents as customarily present in the manufacture of fibers. For example, the fiber may contain various pigments, fillers, delustrants, and the like, which may be added to the polymer or to the reactants forming the polymer. Various types of finishes, resins, antioxidants, water repellents, and other surface-modifying agents may be applied to the filaments after they have been formed.

In the preferred embodiment of this invention in which an inert, low-boiling, soluble fluid is added to the molten polymer prior to spinning, the preferred fluids are the chlorinated hydrocarbons and halogenated hydrocarbons, particularly the chlorofluorinated hydrocarbons. As suitable examples of the preferred fluids useful in the process of this invention may be mentioned CC12FCC12F2, CC1FCC1F2, C2Cl2F4, hexane, heptane, octane, nonane, decane, cyclopentane, and cyclohexane. Other useful fluids include ethyl ether, carbon tetrachloride, 1-chloroethylene, 1,2-dichloroethylene, 1,3-dichloroethane, and benzene. Mixtures of fluids may also be used.

If desired, a suitable fluid may be encapsulated and mixed with polymer flake, before melting, in the encapsulated form.

In the embodiment in which the pulverized superpolymer is melted under pressure of an inert gas or vapor, or in which an inert gas or vapor is introduced into the molten polymer under pressure, any inert material may be employed which is gaseous at the temperature of the molten polymer and which does not react with it to any harmful extent under the conditions of use. Preferably, the gas is soluble in the molten polymer. Thus, there may be used nitrogen, hydrogen, helium, carbon dioxide, methane, ethane, and other nonreactive gases.

In the embodiment of this invention in which the molten polymer contains a solid material capable of decomposing to give a gas at the temperature of extrusion, it is desirable that the solid material and the gas formed from it be chemically inert to the polymer. As suitable examples of such materials may be mentioned zinc carbonate, oxalic acid, dimethyl oxalate, poly(diphenylopropone carbonate), poly(dimethylhydrylic acid) and other compounds which react with dichloroethylene.

In summary, any material may be used which has, or the decomposition products of which have, an appreciable vapor pressure at melt spinning temperatures. It is usually desirable, of course, that neither the materials nor their decomposition products cause degradation or distortion of the substrate.

In the manufacture of hollow fibers by the process of this invention, the shape of the hollow core can be modified by changing the shape of the solid insert in the spinneret orifice. Thus, fibers having various combinations of external and internal cross sectional shapes may be prepared. For example, round filaments having non-round voids such as oval, triangular, square, or star-shaped, may be made. Alternatively, triangular filaments having round or non-round voids may be prepared.
The hollow fibers produced by the practice of this invention are of great advantage in textile applications. They confer greater warmth and covering power than solid filaments at equivalent weights, and confer a different and, for some applications, a more desirable hand to fabrics made therefrom. Those filaments containing more than 10% hollow space by volume are particularly valuable in that, as staple fiber made into worsted-type or cotton-like fabrics, they have a significantly lower tendency to pill than fabrics of solid filaments.

This invention is particularly directed to a process for preparing filaments and yarns (i.e., bundles of filaments, whether continuous filaments or staple fiber) having deniers of the magnitude used in textiles. It is preferred that the filaments of this invention have a denier (per filament) in the range of 1–15 (0.11–1.7 Tex.) and that the yarns of this invention have a denier of 30–8,000 (3.4–890 Tex.). For specialty uses, filament deniers as high as 150 (17 Tex.) may be desirable.

The hollow filaments prepared by the process of this invention may advantageously be made into woven, non-woven, or knitted textiles without blending with other fibers. Alternatively, they may be blended, particularly as staple fibers, with other synthetic or artificial fibers, either solid or hollow, or with natural fibers such as wool, cotton, etc., either by blending in the manufacture of the yarn, or by blending yarns composed only of the filaments and fibers prepared by the process of this invention with yarns of other fibers, during the weaving or knitting operations.

The hollow filaments prepared by the process of this invention are also useful as filling or stuffing materials in pillows, mattresses, upholstery and the like.

The process of this invention provides a simple and inexpensive method of manufacturing hollow filaments from synthetic polymers. The fibers produced are of high quality and possess the advantage that in the case of finished filaments, they have equal outer diameters but much lighter weights than solid filaments, and thus may be made with an appreciably smaller expenditure of material. Furthermore, these filaments possess all the known advantages of hollow filaments, including greater bulk and greater heat insulation potential.

Since many different embodiments of the invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention is not limited by the specific illustrations except to the extent defined in the following claims.

I claim:

1. In the melt-spinning process of extruding molten synthetic linear polymer under pressure through a spinneret orifice to form a filament and quenching to solidify the filament, the improvement for producing a hollow-core filament of extruding a polymer melt which releases gas, as pressure on the polymer decreases during formation of the filament, through a center-obstructed orifice to form a central void surrounded by a continuous unbroken polymer sheath, the quantity of released gas being sufficient to maintain a void in the filament produced which is at least 5% of the cross-sectional area of the filament.

2. A process as defined in claim 1 wherein the polymer melt contains 0.05% to 4.0% by weight, based on the weight of the polymer, of a low-boiling inert liquid which vaporizes upon extrusion of the melt to form said released gas.

3. A process as defined in claim 1 wherein the polymer melt contains inert gas dissolved therein while the melt is under pressure and released upon extrusion of the melt to form a gas volume, at the temperature of extrusion, equal to about 5% to 85% of the volume of the filament.

4. A process as defined in claim 3 wherein said gas is dissolved in the polymer by introducing gas under pressure.

5. A process as defined in claim 3 wherein said gas is formed in the melt by adding a solid material which decomposes to form gas at the temperature of polymer extrusion.

6. A process as defined in claim 5 wherein the solid material is soluble in the molten polymer.

7. A process as defined in claim 1 wherein the center-obstructed orifice is circular and the polymer melt is extruded through an opening in the shape of an annular ring to form a tubular filament.

8. A process as defined in claim 1 wherein the center-obstructed orifice is non-circular and the polymer melt is extruded through a slit extending completely around the perimeter of a solid center obstruction.

9. A process as defined in claim 8 wherein the orifice is triangular.

No references cited.