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Remarks:
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(54) Elastic fibers and fabric

(57) Melt spun elastic fibers are disclosed which can be made into garments having a very comfortable feel. The elastic fibers comprise a polyester thermoplastic polyurethane prepared from a reaction mixture comprising a polyisocyanate, a linear hydroxyl terminated polyester intermediate and one or more chain extenders.

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Description

FIELD OF THE INVENTION

[0001] The present invention relates to high strength fabrics made from thin gauge constant compression elastic fibers. Garments made with the constant compression elastic fibers have a very comfortable feel to the wearer. The garments are also resistant to puncture due to the high strength fabric made with the elastic fibers.

BACKGROUND OF THE INVENTION

[0002] In recent years, the demand for greater functionality in fabrics, over and beyond the basic function of insulation, has been high due to the changing lifestyles across the globe. One such sought after functionality is fabrics of thinner gauges without sacrificing the strength and integrity of the fabric. This thinner gauge fabric allows for lower packing volumes, a reduction of a feeling of "bulk" and in the case of undergarments, a lack of external visibility through the outer garment.

[0003] Synthetic elastic fibers (SEF) are normally made from polymers having soft and hard segments to give elasticity. Polymers having hard and soft segments are typically poly(ether-amide), such as Pebax® or copolyesters, such as Hytrel® or thermoplastic polyurethane, such as Estane®. However, very high elongation SEF typically utilize hard and soft segmented polymers such as dry spun polyurethane (Lycra®) or melt spun thermoplastic polyurethane (Estane®). While these SEF vary, from low to very high, in elongation of break, all can be commonly described as having an exponentially increasing modulus (strain) with an increase in elongation (stress).

[0004] Melt spun TPU fibers offer some advantages over dry spun polyurethane fibers in that no solvent is used in the melt spun process, whereas in the dry spinning process, the polymer is dissolved in solvent and spun. The solvent is then partially evaporated out of the fibers. All of the solvent is very difficult to completely remove from the dry spun fibers. To facilitate removing the solvent from dry spun fibers, they are typically made into a small size and bunched together to create a multi-filament (ribbon-like) fiber. This results in a larger physical size for a given denier as compared to a melt spun fiber. These physical characteristics results in more bulk in the fabric and the nature of the multi-filament bundle contributes to a loss of comfort.

[0005] Melt spun TPU fibers are made by melt spinning a TPU polymer. TPU polymers are made from the reaction of three components, i.e., (a) a hydroxyl terminated intermediate, which is typically a polyether or polyester end capped with a hydroxyl group; (b) a polyisocyanate, such as a diisocyanate; and (c) a short chain hydroxyl terminated chain extender. The hydroxyl terminated intermediate forms the soft segment of the TPU polymer while the polyisocyanate and the chain extender forms the hard segment of the TPU polymer. The combination of soft and hard segments gives the TPU polymer elastic properties. The TPU polymer is also frequently lightly crosslinked by using a pre-polymer end capped with a polyisocyanate to give enhanced properties. The crosslinking material is added to the melted TPU polymer during melt spinning of the fiber.

[0006] It would be desirable to have a TPU elastic fiber which has a relatively constant compression between zero and 250% elongation and to make constant compression garments and/or fabrics containing such TPU fibers. Also, it would be desirable for these constant compression fabrics to be thin gauge and to have a high puncture resistance. Garments made from such fabrics would offer more comfort and confidence to the wearer.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] Figure 1 is a photo micrograph of a 70 denier multi-filament of a commercial dry spun polyurethane fiber.

[0008] Figure 2 is a photo micrograph of a 70 denier of a melt spun constant compression thermoplastic polyurethane fiber of the present invention.

[0009] Figure 3 is a graph showing the X axis as denier vs. the Y axis of fiber width squared (square microns). The fiber of this invention is compared to a commercial dry spun fiber.

SUMMARY OF THE INVENTION

[0010] It is an object of the present invention to provide a thin gauge, constant compression, high strength fiber having an ultimate elongation of at least 400% and having a relatively flat and/or constant modulus in the load and unload cycle between 100% and 200% elongation. This flat and/or constant modulus is evidenced by a stress in the load cycle at 100% elongation of less than 0.023 gram-force per denier, at 150% elongation of less than 0.023 gram-force per denier, at 200% elongation of less than 0.053 gram-force per denier; and as evidenced by a stress in the unload cycle at 200% elongation of less than 0.027 gram-force per denier, at 150% elongation of less than 0.018 gram-force per denier, and at 100% elongation of less than 0.015 gram-force per denier.

[0011] An exemplary fiber is made by melt spinning a thermoplastic polyurethane polymer, preferably a polyester polyurethane polymer. The fiber is lightly crosslinked by adding a crosslinking agent, preferably 5 to 20 weight percent, to the polymer melt during the melt spinning process.

[0012] A process to produce the fiber involves a melt spinning process whereby the fiber is formed by passing the polymer melt through a spinneret. The velocity of the fiber exiting the spinneret and the velocity at which the fiber is wound into bobbins is relatively close. That is, the fibers should be wound into bobbins at a speed no more than 50%, preferably 20%, and more preferably 10%, greater than the speed at which the fiber is exiting the spinneret.

[0013] It is another object of the invention to produce fabric with the thin gauge, constant compression fiber. In an exemplary embodiment, the fabric is made by combining, such as by knitting or weaving, the elastic fiber with a hard fiber, such as nylon and/or polyester fiber. Fabric made with the novel fiber also has high burst strength.

[0014] Clothing garments, such as undergarments, are made from the elastic fiber. Such garments offer very good comfort to the wearer.

DETAILED DESCRIPTION OF THE INVENTION

[0015] The fiber of this invention is made from a thermoplastic elastomer. The preferred thermoplastic elastomer is a thermoplastic polyurethane polymer (TPU). The invention will be described using a TPU, but it should be understood that this is only one embodiment and other thermoplastic elastomers can be used by those skilled in the art.

[0016] The TPU polymer type used in this invention can be any conventional TPU polymer that is known to the art and in the literature as long as the TPU polymer has adequate molecular weight. The TPU polymer is generally prepared by reacting a polyisocyanate with an intermediate such as a hydroxyl terminated polyester, a hydroxyl terminated polyether, a hydroxyl terminated polycarbonate or mixtures thereof, with one or more chain extenders, all of which are well known to those skilled in the art.

[0017] The hydroxyl terminated polyester intermediate is generally a linear polyester having a number average molecular weight (Mn) of from about 500 to about 10,000, desirably from about 700 to about 5,000, and preferably from about 700 to about 4,000, an acid number generally less than 1.3 and preferably less than 0.8. The molecular weight is determined by assay of the terminal functional groups and is related to the number average molecular weight. The polymers are produced by (1) an esterification reaction of one or more glycols with one or more dicarboxylic acids or anhydrides or (2) by transesterification reaction, i.e., the reaction of one or more glycols with esters of dicarboxylic acids. Mole ratios generally in excess of more than one mole of glycol to acid are preferred so as to obtain linear chains having a preponderance of terminal hydroxyl groups. Suitable polyester intermediates also include various lactones such as polycaprolactone typically made from ε-caprolactone and a bifunctional initiator such as diethylene glycol. The dicarboxylic acids of the desired polyester can be aliphatic, cycloaliphatic, aromatic, or combinations thereof. Suitable dicarboxylic acids which may be used alone or in mixtures generally have a total of from 4 to 15 carbon atoms and include: succinic, glutaric, adipic, pimelic, suberic, azelaic, sebacic, dodecanedioic, isophthalic, terephthalic, cyclohexane dicarboxylic, and the like. Anhydrides of the above dicarboxylic acids such as phthalic anhydride, tetrahydrophthalic anhydride, or the like, can also be used. Adipic acid is the preferred acid. The glycols which are reacted to form a desirable polyester intermediate can be aliphatic, aromatic, or combinations thereof, and have a total of from 2 to 12 carbon atoms, and include ethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 2,2-dimethyl-1,3-propanediol, 1,4-cyclohexanedimethanol, decamethylene glycol, dodecamethylene glycol, and the like, 1,4-butanediol is the preferred glycol.

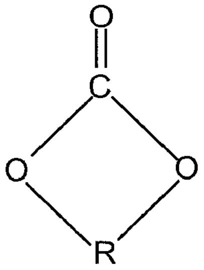
[0018] Hydroxyl terminated polyether intermediates are polyether polyols derived from a diol or polyol having a total of from 2 to 15 carbon atoms, preferably an alkyl diol or glycol which is reacted with an ether comprising an alkylene oxide having from 2 to 6 carbon atoms, typically ethylene oxide or propylene oxide or mixtures thereof. For example, hydroxyl functional polyether can be produced by first reacting propylene glycol with propylene oxide followed by subsequent reaction with ethylene oxide. Primary hydroxyl groups resulting from ethylene oxide are more reactive than secondary hydroxyl groups and thus are preferred. Useful commercial polyether polyols include poly(ethylene glycol) comprising ethylene oxide reacted with ethylene glycol, poly(propylene glycol) comprising propylene oxide reacted with propylene glycol, poly(tetramethyl glycol) comprising water reacted with tetrahydrofuran (PTMEG). Polytetramethylene ether glycol (PTMEG) is the preferred polyether intermediate. Polyether polyols further include polyamide adducts of an alkylene oxide and can include, for example, ethylenediamine adduct comprising the reaction product of ethylenediamine and propylene oxide, diethylenetriamine adduct comprising the reaction product of diethylenetriamine with propylene oxide, and similar polyamide type polyether polyols. Copolyethers can also be utilized in the current invention. Typical copolyethers include the reaction product of THF and ethylene oxide or THF and propylene oxide. These are available from BASF as Poly THF B, a block copolymer, and poly THF R, a random copolymer. The various polyether intermediates generally have a number average molecular weight (Mn) as determined by assay of the terminal functional groups which is an average molecular weight greater than about 700, such as from about 700 to about 10,000, desirably from about 1000 to about 5000, and preferably from about 1000 to about 2500. A particular desirable polyether intermediate is a blend of two or more different molecular weight polyethers, such as a blend of 2000 M_n and 1000 M_n PTMEG.

[0019] The most preferred embodiment of this invention uses a polyester intermediate made from the reaction of adipic acid with a 50/50 blend of 1,4-butanediol and 1,6-hexanediol.

[0020] The polycarbonate-based polyurethane resin of this invention is prepared by reacting a diisocyanate with a blend of a hydroxyl terminated polycarbonate and a chain extender. The hydroxyl terminated polycarbonate can be prepared by reacting a glycol with a carbonate.

[0021] U.S. Patent No. 4,131,731 is hereby incorporated by reference for its disclosure of hydroxyl terminated polycarbonates and their preparation. Such polycarbonates are linear and have terminal hydroxyl groups with essential exclusion of other terminal groups. The essential reactants are glycols and carbonates. Suitable glycols are selected from cycloaliphatic and aliphatic diols containing 4 to 40, and preferably 4 to 12 carbon atoms, and from polyoxyalkylene glycols containing 2 to 20 alkoxy groups per molecular with each alkoxy group containing 2 to 4 carbon atoms. Diols suitable for use in the present invention include aliphatic diols containing 4 to 12 carbon atoms such as butanediol-1,4, pentanediol-1,4, neopentyl glycol, hexanediol-1,6, 2,2,4-trimethylhexanediol-1,6, decanediol-1,10, hydrogenated dilinoleylglycol, hydrogenated dioleylglycol; and cycloaliphatic diols such as cyclohexanediol-1,3, dimethylolcyclohexane-1,4, cyclohexanediol-1,4, dimethylolcyclohexane-1,3, 1,4-endomethylene-2-hydroxy-5-hydroxymethyl cyclohexane, and polyalkylene glycols. The diols used in the reaction may be a single diol or a mixture of diols depending on the properties desired in the finished product.

[0022] Polycarbonate intermediates which are hydroxyl terminated are generally those known to the art and in the literature. Suitable carbonates are selected from alkylene carbonates composed of a 5 to 7 membered ring having the following general formula:



where R is a saturated divalent radical containing 2 to 6 linear carbon atoms. Suitable carbonates for use herein include ethylene carbonate, trimethylene carbonate, tetramethylene carbonate, 1,2-propylene carbonate, 1,2-butylene carbonate, 2,3-butylene carbonate, 1,2-ethylene carbonate, 1,3-pentylene carbonate, 1,4-pentylene carbonate, 2,3-pentylene carbonate, and 2,4-pentylene carbonate.

[0023] Also, suitable herein are dialkylcarbonates, cycloaliphatic carbonates, and diarylcarbonates. The dialkylcarbonates can contain 2 to 5 carbon atoms in each alkyl group and specific examples thereof are diethylcarbonate and dipropylcarbonate. Cycloaliphatic carbonates, especially dicycloaliphatic carbonates, can contain 4 to 7 carbon atoms in each cyclic structure, and there can be one or two of such structures. When one group is cycloaliphatic, the other can be either alkyl or aryl. On the other hand, if one group is aryl, the other can be alkyl or cycloaliphatic. Preferred examples of diarylcarbonates, which can contain 6 to 20 carbon atoms in each aryl group, are diphenylcarbonate, ditolylcarbonate, and dinaphthylcarbonate.

[0024] The reaction is carried out by reacting a glycol with a carbonate, preferably an alkylene carbonate in the molar range of 10:1 1 to 1:10, but preferably 3:1 to 1:3 at a temperature of 100°C to 300°C and at a pressure in the range of 0.1 to 300 mm of mercury in the presence or absence of an ester interchange catalyst, while removing low boiling glycols by distillation.

[0025] More specifically, the hydroxyl terminated polycarbonates are prepared in two stages. In the first stage, a glycol is reacted with an alkylene carbonate to form a low molecular weight hydroxyl terminated polycarbonate. The lower boiling point glycol is removed by distillation at 100°C to 300°C, preferably at 150°C to 250°C, under a reduced pressure of 10 to 30 mm Hg, preferably 50 to 200 mm Hg. A fractionating column is used to separate the by-product glycol from the reaction mixture. The by-product glycol is taken off the top of the column and the unreacted alkylene carbonate and glycol reactant are returned to the reaction vessel as reflux. A current of inert gas or an inert solvent can be used to facilitate removal of by-product glycol as it is formed. When amount of by-product glycol obtained indicates that degree of polymerization of the hydroxyl terminated polycarbonate is in the range of 2 to 10, the pressure is gradually reduced to 0.1 to 10 mm Hg and the unreacted glycol and alkylene carbonate are removed. This marks the beginning of the second stage of reaction during which the low molecular weight hydroxyl terminated polycarbonate is condensed by distilling off glycol as it is formed at 100°C to 300°C, preferably 150°C to 250°C and at a pressure of 0.1 to 10 mm Hg until the desired molecular weight of the hydroxyl terminated polycarbonate is attained. Molecular weight (Mn) of the hydroxyl terminated polycarbonates can vary from about 500 to about 10,000 but in a preferred embodiment, it will be in the range of 500 to 2500.

[0026] The second necessary ingredient to make the TPU polymer of this invention is a polyisocyanate.

[0027] The polyisocyanates of the present invention generally have the formula $R(NCO)_n$ where n is generally from 2 to 4 with 2 being highly preferred inasmuch as the composition is a thermoplastic. Thus, polyisocyanates having a functionality of 3 or 4 are utilized in very small amounts, for example less than 5% and desirably less than 2% by weight based upon the total weight of all polyisocyanates, inasmuch as they cause crosslinking. R can be aromatic, cycloaliphatic, and aliphatic, or combinations thereof generally having a total of from 2 to about 20 carbon atoms. Examples of suitable aromatic diisocyanates include diphenyl methane-4, 4'-diisocyanate (MDI), H_{12} MDI, m-xylylene diisocyanate (XDI), m-tetramethyl xylylene diisocyanate (TMXDI), phenylene-1, 4-diisocyanate (PPDI), 1,5-naphthalene diisocyanate (NDI), and diphenylmethane-3, 3'-dimethoxy-4, 4'-diisocyanate (TODI). Examples of suitable aliphatic diisocyanates include isophorone diisocyanate (IPDI), 1,4-cyclohexyl diisocyanate (CHDI), hexamethylene diisocyanate (HDI), 1,6-diisocyanato-2,2,4,4-tetramethyl hexane (TMDI), 1,10-decane diisocyanate, and trans-dicyclohexylmethane diisocyanate (HMDI). A highly preferred diisocyanate is MDI containing less than about 3% by weight of ortho-para (2,4) isomer.

[0028] The third necessary ingredient to make the TPU polymer of this invention is the chain extender. Suitable chain extenders are lower aliphatic or short chain glycols having from about 2 to about 10 carbon atoms and include for instance ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, triethylene glycol, cis-trans-isomers of cyclohexyl dimethylol, neopentyl glycol, 1,4-butanediol, 1,6-hexandiol, 1,3-butanediol, and 1,5-pentanediol. Aromatic glycols can also be used as the chain extender and are the preferred choice for high heat applications. Benzene glycol (HQEE) and xylenene glycols are suitable chain extenders for use in making the TPU of this invention. Xylenene glycol is a mixture of 1,4-di(hydroxymethyl) benzene and 1,2-di(hydroxymethyl) benzene. Benzene glycol is the preferred aromatic chain extender and specifically includes hydroquinone, i.e., bis(beta-hydroxyethyl) ether also known as 1,4-di (2-hydroxyethoxy) benzene; resorcinol, i.e., bis(beta-hydroxyethyl) ether also known as 1,3-di(2-hydroxyethyl) benzene; catechol, i.e., bis(beta-hydroxyethyl) ether also known as 1,2-di(2-hydroxyethoxy) benzene; and combinations thereof. The preferred chain extender is 1,4-butanediol.

[0029] The above three necessary ingredients (hydroxyl terminated intermediate, polyisocyanate, and chain extender) are preferably reacted in the presence of a catalyst.

[0030] Generally, any conventional catalyst can be utilized to react the diisocyanate with the hydroxyl terminated intermediate or the chain extender and the same is well known to the art and to the literature. Examples of suitable catalysts include the various alkyl ethers or alkyl thiol ethers of bismuth or tin wherein the alkyl portion has from 1 to about 20 carbon atoms with specific examples including bismuth octoate, bismuth laurate, and the like. Preferred catalysts include the various tin catalysts such as stannous octoate, dibutyltin dioctoate, dibutyltin dilaurate, and the like. The amount of such catalyst is generally small such as from about 20 to about 200 parts per million based upon the total weight of the polyurethane forming monomers.

[0031] The TPU polymers of this invention can be made by any of the conventional polymerization methods well known in the art and literature.

[0032] Thermoplastic polyurethanes of the present invention are preferably made via a "one shot" process wherein all the components are added together simultaneously or substantially simultaneously to a heated extruder and reacted to form the polyurethane. The equivalent ratio of the diisocyanate to the total equivalents of the hydroxyl terminated intermediate and the diol chain extender is generally from about 0.95 to about 1.10, desirably from about 0.97 to about 1.03, and preferably from about 0.97 to about 1.00. The Shore A hardness of the TPU formed should be from 65A to 95A, and preferably from about 75A to about 85A, to achieve the most desirable properties of the finished article. Reaction temperatures utilizing urethane catalyst are generally from about 175°C to about 245°C and preferably from about 180°C to about 220°C. The molecular weight (Mw) of the thermoplastic polyurethane is generally from about 100,000 to about 800,000 and desirably from about 150,000 to about 400,000 and preferably about 150,000 to about 350,000 as measured by GPC relative to polystyrene standards.

[0033] The thermoplastic polyurethanes can also be prepared utilizing a pre-polymer process. In the pre-polymer route, the hydroxyl terminated intermediate is reacted with generally an equivalent excess of one or more polyisocyanates to form a pre-polymer solution having free or unreacted polyisocyanate therein. Reaction is generally carried out at temperatures of from about 80°C to about 220°C and preferably from about 150°C to about 200°C in the presence of a suitable urethane catalyst. Subsequently, a selective type of chain extender as noted above is added in an equivalent amount generally equal to the isocyanate end groups as well as to any free or unreacted diisocyanate compounds. The overall equivalent ratio of the total diisocyanate to the total equivalent of the hydroxyl terminated intermediate and the chain extender is thus from about 0.95 to about 1.10, desirably from about 0.98 to about 1.05 and preferably from about 0.99 to about 1.03. The equivalent ratio of the hydroxyl terminated intermediate to the chain extender is adjusted to give 65A to 95A, preferably 75A to 85A Shore hardness. The chain extension reaction temperature is generally from about 180°C to about 250°C with from about 200°C to about 240°C being preferred. Typically, the pre-polymer route can be carried out in any conventional device with an extruder being preferred. Thus, the hydroxyl terminated intermediate is reacted with an equivalent excess of a diisocyanate in a first portion of the extruder to form a pre-polymer solution and subsequently the chain extender is added at a downstream portion and reacted with the pre-polymer solution. Any conventional extruder can be utilized, with extruders equipped with barrier screws having a length to diameter ratio of at least 20 and preferably at least 25.

[0034] Useful additives can be utilized in suitable amounts and include opacifying pigments, colorants, mineral fillers, stabilizers, lubricants, UV absorbers, processing aids, and other additives as desired. Useful opacifying pigments include titanium dioxide, zinc oxide, and titanate yellow, while useful tinting pigments include carbon black, yellow oxides, brown oxides, raw and burnt sienna or umber, chromium oxide green, cadmium pigments, chromium pigments, and other mixed metal oxide and organic pigments. Useful fillers include diatomaceous earth (superfloss) clay, silica, talc, mica, wallostonite, barium sulfate, and calcium carbonate. If desired, useful stabilizers such as antioxidants can be used and include phenolic antioxidants, while useful photostabilizers include organic phosphates, and organotin thiolates (mercaptides). Useful lubricants include metal stearates, paraffin oils and amide waxes. Useful UV absorbers include 2-(2'-hydroxyphenol) benzotriazoles and 2-hydroxybenzophenones.

[0035] Plasticizer additives can also be utilized advantageously to reduce hardness without affecting properties.

[0036] During the melt spinning process, the TPU polymer described above may be lightly crosslinked with a crosslinking agent. The crosslinking agent is a pre-polymer of a hydroxyl terminated intermediate that is a polyether, polyester, polycarbonate, polycaprolactone, or mixture thereof reacted with a polyisocyanate. A polyester or polyether are the preferred hydroxyl terminated intermediates to make the crosslinking agent, with a polyether being the most preferred when used in combination with a polyester TPU. The crosslinking agent, pre-polymer, will have an isocyanate functionality of greater than about 1.0, preferably from about 1.0 to about 3.0, and more preferably from about 1.8 to about 2.2. It is particularly preferred if both ends of hydroxyl terminated intermediate is capped with an isocyanate, thus having an isocyanate functionality of 2.0.

[0037] The polyisocyanate used to make the crosslinking agent are the same as described above in making the TPU polymer. A diisocyanate, such as MDI, is the preferred diisocyanate.

[0038] The crosslinking agents have a number average molecular weight (Mn) of from about 1,000 to about 10,000 Daltons, preferably from about 1,200 to about 4,000 and more preferably from about 1,500 to about 2,800. Crosslinking agents with above about 1500 M_n give better set properties.

[0039] The weight percent of crosslinking agent used with the TPU polymer is from about 2.0% to about 20%, preferably about 8.0% to about 15%, and more preferably from about 10% to about 13%. The percentage of crosslinking agent used is weight percent based upon the total weight of TPU polymer and crosslinking agent.

[0040] The preferred melt spinning process to make TPU fibers of this invention involves feeding a preformed TPU polymer to an extruder, to melt the TPU polymer and the crosslinking agent is added continuously downstream near the point where the TPU melt exits the extruder or after the TPU melt exits the extruder. The crosslinking agent can be added to the extruder before the melt exits the extruder or after the melt exits the extruder. If added after the melt exits the extruder, the crosslinking agent needs to be mixed with the TPU melt using static or dynamic mixers to assure proper mixing of the crosslinking agent into the TPU polymer melt. After exiting the extruder, the melted TPU polymer with crosslinking agent flows into a manifold. The manifold divides the melt stream into different streams, where each stream is fed to a plurality of spinnerets. Usually, there is a melt pump for each different stream flowing from the manifold, with each melt pump feeding several spinnerets. The spinneret will have a small hole through which the melt is forced and exits the spinneret in the form of a monofilament fiber. The size of the hole in the spinneret will depend on the desired size (denier) of the fiber.

[0041] The TPU polymer melt may be_passed through a spin pack assembly and exits the spin pack assembly used as a fiber. The preferred spin pack assembly used is one which gives plug flow of the TPU polymer through the assembly. The most preferred spin pack assembly is the one described in PCT patent application WO 2007/076380, which is incorporated in its entirety herein.

[0042] Once the fiber exits the spinneret, it is cooled before winding onto bobbins. The fiber is passed over a first godet, finish oil is applied, and the fiber proceeds to a second godet. An important aspect of the process to make the fiber of this invention is the relative speed at which the fiber is wound into bobbins. By relative speed, we mean the speed of the melt (melt velocity) exiting the spinneret in relationship to the winding speed. In a normal prior art TPU melt spinning process, the fiber is wound at a speed of 4-6 times the speed of the melt velocity. This draws or stretches the fiber. For the unique fibers of this invention, this extensive drawing is undesirable. The fibers must be wound at a speed at least equal to the melt velocity to operate the process. For the fibers of this invention, it is necessary to wind the fibers at a speed no greater than 50% faster than the melt velocity, preferably no greater than 20%, and more preferably no greater than 10%, with no greater than 5% giving excellent results. It is thought that a winding speed that is the same as the melt velocity would be ideal, but it is necessary to have a slightly higher winding speed to operate the process. For example, a fiber exiting the spinneret at a speed of 300 meters per minute, would most preferable be wound at a speed of between 300 and 315 meters per minute.

[0043] The fibers of this invention can be made in a variety of denier. Denier is a term in the art designating the fiber size. Denier is the weight in grams of 9000 meters of fiber length. The fibers of this invention are typically made in sizes ranging from 20 to 600 denier, preferably 40 to 400, and more preferably 70 to 360 denier.

[0044] When fibers are made by the process of this invention, anti-tack additives such as finish oils, an example of which are silicone oils, are usually added to the surface of the fibers after or during cooling and just prior to being wound into bobbins.

[0045] An important aspect of the melt spinning process is the mixing of the TPU polymer melt with the crosslinking agent. Proper uniform mixing is important to achieve uniform fiber properties and to achieve long run times without experiencing fiber breakage. The mixing of the TPU melt and crosslinking agent should be a method which achieves plug-flow, i.e., first in first out. The proper mixing can be achieved with a dynamic mixer or a static mixer. Static mixers are more difficult to clean; therefore, a dynamic mixer is preferred. A dynamic mixer which has a feed screw and mixing pins is the preferred mixer. U.S. Patent 6,709,147, which is incorporated herein by reference, describes such a mixer and has mixing pins which can rotate. The mixing pins can also be in a fixed position, such as attached to the barrel of the mixer and extending toward the centerline of the feed screw. The mixing feed screw can be attached by threads to the end of the extruder screw and the housing of the mixer can be bolted to the extruder machine. The feed screw of the dynamic mixer should be a design which moves the polymer melt in a progressive manner with very little back mixing to achieve plug-flow of the melt. The L/D of the mixing screw should be from over 3 to less than 30, preferably from about 7 to about 20, and more preferably from about 10 to about 12.

[0046] The temperature in the mixing zone where the TPU polymer melt is mixed with the crosslinking agent is from about 200°C to about 240°C, preferably from about 210°C to about 225°C. These temperatures are necessary to get the reaction while not degrading the polymer.

[0047] The TPU formed is reacted with the crosslinking agent during the melt spinning process to give a molecular weight (Mw) of the TPU in final fiber form, of from about 200,000 to about 800,000, preferably from about 250,000 to about 500,000, more preferably from about 300,000 to about 450,000.

[0048] The spinning temperature (the temperature of the polymer melt in the spinneret) should be higher than the melting point of the polymer, and preferably from about 10°C to about 20°C above the melting point of the polymer. The higher the spinning temperature one can use, the better the spinning. However, if the spinning temperature is too high, the polymer can degrade. Therefore, from about 10°C to about 20°C above the melting point of the TPU polymer, is the optimum for achieving a balance of good spinning without degradation of the polymer. If the spinning temperature is too low, polymer can solidify in the spinneret and cause fiber breakage.

[0049] The unique fiber of this invention has a relatively flat and/or constant modulus in the load and unload cycle between 100% and 200% elongation. This flat modulus is evidenced by a stress in the load cycle at 100% elongation of less than 0.023 gram-force per denier, at 150% elongation of less than 0.036 gram-force per denier, at 200% elongation of less than 0.053 gram-force per denier; and as evidenced by a stress in the unload cycle at 200% elongation of less than 0.027 gram-force per denier, at 150% elongation of less than 0.018 gram-force per denier, and at 100% elongation of less than 0.015 gram-force per denier, where all of this data was collected from a 360 denier fiber.

[0050] This flat modulus is also evidenced by a stress in the load cycle at 100% elongation of less than 0.158 gram-force per denier, at 150% elongation of less than 0.207 gram-force per denier, at 200% elongation of less than 0.265 gram-force per denier; and as evidenced by a stress in the unload cycle at 200% elongation of less than 0.021 gram-force per denier, at 150% elongation of less than 0.012 gram-force per denier, and at 100% elongation of less than 0.008 gram-force per denier, where all of this data was collected from a 70 denier fiber.

[0051] The standard test procedure employed to obtain the modulus values above is one which was developed by DuPont for elastic yarns. The test subjects fibers to a series of 5 cycles. In each cycle, the fiber is stretched to 300% elongation, and relaxed using a constant extension rate (between the original gauge length and 300% elongation). The % set is measured after the 5th cycle. Then, the fiber specimen is taken through a 6th cycle and stretched to breaking. The instrument records the load at each extension, the highest load before breaking, and the breaking load in units of grams-force per denier as well as the breaking elongation and elongation at the maximum load. The test is normally conducted at room temperature (23°C ± 2°C; and 50% ± 5% humidity).

[0052] The fiber of this invention has an elongation at break of at least 400%, and preferably about 450 to 500%. The fiber is a monofilament with a round shape. Referring to FIG. 2, it can be seen that a 70 denier monofilament fiber is substantially round in cross sectional shape. FIG. 1 shows a 70 denier monofilament dry spun fiber which has a larger cross section width.

[0053] FIG. 3 shows a graph comparing a dry spun fiber with the melt spun fiber of this invention. The graph plots the denier (X axis) vs. the fiber width squared (square microns). The graph shows that the melt spun fiber of this invention has a constant slope on the graph, whereas the dry spun fiber has an expotentially increasing slope. The result is that fabric can be made with the fiber of this invention which is thinner and thus more comfortable for the wearer.

[0054] Another important feature of the fiber of this invention is that it exhibits improved burst strength in fabric compared to dry spun fibers.

[0055] This feature can be shown by performing the Ball Burst Puncture Strength Test according to ASTM D751 using a 1 inch diameter ball. This test would simulate a finger pushing through the fabric to form a hole. It was very surprising that the fibers of this invention show about a 50 to 75% improvement in burst strength as compared to dry spun polyurethane fiber. This improved burst strength exists even though the tensile strength of the fiber is almost the same.

[0056] The fiber of this invention also has higher heat capacity. The combination of flat modulus curve, higher heat capacity, and thinner gauge results in fabric made with the fibers of this invention feeling comfortable to the wearer of garments.

[0057] Fabric made using the fibers of this invention can be made by knitting or weaving. Often it is preferred to make fabric using other fibers with the TPU fibers. Particularly preferred is to use a hard fiber with the elastic fibers of this invention. Hard fibers, such as nylon and/or polyester are preferred. The hard fibers improve the snag resistance of the fabric over a 100% elastic fiber fabric. A preferred fabric is one knitted using alternating fibers, such as a strand of 140 denier TPU/70 denier nylon alternating with a strand of 140 denier TPU (referred to as a 1-1 fabric) or a strand of 140 denier TPU/70 denier nylon followed by 2 strands of 140 denier TPU (referred to as 1-2 fabric).

[0058] Garments can be made with the fabric of this invention. The most preferred use of the fabric is in making undergarments or tight fitting garments because of the comfort provided by the fiber. Undergarments, such as bras and T-shirts as well as sport garments used for activities such as running, skiing, cycling or other sports, can benefit from the properties of these fibers. Garments worn next to the body benefit from the flat modulus of these fibers, because the modulus is even lower once the fibers reach body temperature. A garment that feels tight will become more comfortable in about 30 seconds to 5 minutes after the fibers reach body temperature. It will be understood by those skilled in the art that any garment can be made from the fabric and fibers of this invention. An exemplary embodiment would be a bra shoulder strap made from woven fabric and the wings of the bra made from knitted fabric, with both the woven and the knitted fabric containing the melt spun TPU fibers of this invention. The bra strap would not require an adjustable clasp because the fabric is elastic.

[0059] The invention will be better understood by reference to the following examples.

EXAMPLES

[0060] The TPU polymer used in the Examples was made by reacting a polyester hydroxyl terminated intermediate (polyol) with 1,4-butanediol chain extender and MDI. The polyester polyol was made by reacting adipic acid with a 50/50 mixture of 1,4-butanediol and 1,6-hexanediol. The polyol had a Mn of 2500. The TPU was made by the one-shot process. The crosslinking agent added to the TPU during the spinning process was a polyether pre-polymer made by reacting 1000 Mn PTMEG with MDI to create a polyether end capped with isocyanate. The crosslinking agent was used at a level of 10 wt.% of the combined weight of TPU plus crosslinking agent. Fiber were melt spun to make 40, 70, 140 and 360 denier fibers used in the Examples.

EXAMPLE 1

[0061] This Example is presented to show the relative flat modulus curve of the fiber (70 denier) of this invention as compared to an existing prior art melt spun TPU fiber (40 denier) and a commercial dry spun fiber (70 denier).

[0062] The test procedure used was that described above for testing elastic properties. An Instron Model 5564 tensiometer with Merlin Software was used. The test conditions were at 23°C ± 2°C and 50% ± 5% humidity. Fiber length of test specimens were 50.0 mm. Four specimens were tested and the results are the mean value of the 4 specimens tested. The results are shown in Table I.

TABLE I

	Units	70 Denier Dry Spun	Prior Art Melt Spun (40 Denier)	This Invention 70 Denier
1st Load Pull @ 100%	g/denier	0.086	0.128	0.157
1st Load Pull @ 150%	g/denier	0.127	0.201	0.206
1st Load Pull @ 200%	g/denier	0.174	0.319	0.264
1st Load Pull @ 300%	g/denier	0.334	0.749	0.497
1st Unload Pull @ 200%	g/denier	0.028	0.035	0.020
1st Unload Pull @ 150%	g/denier	0.017	0.021	0.011
1st Unload Pull @ 100%	g/denier	0.015	0.015	0.007

(continued)

	Units	70 Denier Dry Spun	Prior Art Melt Spun (40 Denier)	This Invention 70 Denier
% Set After 1st Pull	g/denier	39.36%	17.46%	63.89%
5th Load Pull @ 100%	g/denier	0.027	0.028	0.017
5th Load Pull @ 150%	g/denier	0.042	0.043	0.028
5th Load Pull @ 200%	g/denier	0.060	0.064	0.043
5th Load Pull @ 300%	g/denier	0.248	0.442	0.266
5th Unload Pull @ 200%	g/denier	0.028	0.036	0.020
5th Unload Pull @ 150%	g/denier	0.018	0.022	0.012
5th Unload Pull @ 100%	g/denier	0.016	0.017	0.009
% Set After 5th Pull	g/denier	47.49%	26.76%	71.05%
6th Load Pull Break Load	g/denier	1.802	1.876	1.21
6th Load Pull Break Elongation	g/denier	583.74%	469.31%	450.6%

All of the above data are a mean value for 4 specimens tested.

[0063] From the above data, it can be seen that the melt spun fibers of this invention have a relative flat modulus curve during the 5th testing cycle. The first cycle is usually disregarded as this is relieving stress in the fiber.

EXAMPLE 2

[0064] This Example is presented to show the width of a melt spun fiber of this invention as compared to a commercial dry spun fiber. The width was determined by SEM. The results are shown in Table II.

TABLE II

	Fiber Width (Microns)	
Denier	Melt Spun (This Invention)	Dry Spun
10		34.57
20	48.32	69.32
40	73.30	117.58
70	89.23	228.43
140	127.92	--
360	198.38	--

[0065] As can be seen, the dry spun fiber has a much higher width and the difference becomes larger as the denier increases.

EXAMPLE 3

[0066] This Example is presented to show the improved burst strength of the melt spun TPU fiber of this invention as compared to a commercial dry spun polyurethane fiber. 70 denier fibers were used to prepare a signel Jersey knit fabric from each type of fiber. The fabric was tested for burst puncture strength according to ASTM D751. The results are shown in Table III. The results are a mean of 5 samples tested.

TABLE III

Test	Dry Spun	Melt Spun
Load at Failure (lbs)	5.78	9.03
Displacement at Failure (in.)	8.7	10.6
Load/Thick at Failure (lbf/in.)	705	1250
Energy to Failure (lbf-in)	23.0	40.8

[0067] It was very surprising that although the melt spun fibers of this invention did not have higher tensile strength than the dry spun fibers, the burst strength of the melt spun fibers were higher.

[0068] While in accordance with the Patent statutes, the best mode and preferred embodiment has been set forth, the scope of the invention is not limited thereto, but rather by the scope of the attached claims.

1. A thin gauge, constant compression, high burst strength elastic fiber having an ultimate elongation of at least 400% and having a relativity flat modulus in the load and unload cycle between 100% and 200% elongation.

2. The fiber of 1 wherein a 40 denier monofilament fiber has a width of less than 100 microns.

3. The fiber of 1, wherein when said fiber having a denier of 70 is made into a fabric and said fabric is tested for puncture strength according to ASTM D751 said fabric has a load at failure of greater than 6 pounds.

4. The fiber of 1, wherein said fiber is a thermoplastic polyurethane fiber.

5. The fiber of 4, wherein said fiber is a polyester thermoplastic polyurethane.

6. The fiber of 5, wherein said fiber is crosslinked with a polyether crosslinking agent.

7. The fiber of 5, wherein said polyester thermoplastic polyurethane has a weight average molecular weight of from 200,000 to 700,000 Daltons.

8. The fiber of 6, wherein said crosslinking agent is from 5 to 20 weight percent of the combined weight of said polyester thermoplastic polyurethane and said crosslinking agent.

9. The fiber of 8, wherein said crosslinking agent is from 8 to 12 weight percent of the combined weight of said polyester thermoplastic polyurethane and said crosslinking agent.

10. A fabric comprising at least two different fibers wherein at least one of said fibers is a thermoplastic polyurethane fiber and at least one of said fibers is a hard fiber, and wherein said thermoplastic polyurethane fiber has a relatively flat stress-strain curve between 100 and 200 percent elongation.

11. The fabric of 10, wherein said fabric is made up of two strands of thermoplastic polyurethane fiber for every one strand of hard fiber.

12. The fabric of 10, wherein said thermoplastic polyurethane fiber has a denier of from 20 to 600.

13. The fabric of 12, wherein said thermoplastic polyurethane fiber has a denier of from 70 to 360.

14. The fabric of 10, wherein said hard fiber is selected from the group consisting of Nylon and polyester.

15. The fabric of 14, wherein said hard fiber has a denier of about 70 and said thermoplastic polyurethane fiber has a denier of about 140.

16. An article of clothing comprising the fabric of 10.

17. The article of clothing of 16, wherein said article is an undergarment.

18. The article of clothing of 17, wherein said article is a bra.

19. A process for producing an elastic fiber having a relatively flat modulus in the load and unload cycle between 100% and 200% elongation, said process comprising:

(a) melt spinning a thermoplastic elastomer polymer through a spinneret; and
(b) winding the elastic fiber into bobbins at a winding speed which is no greater than 50% of the polymer melt velocity exiting the spinneret.

20. The process of 19, wherein said winding speed is no greater than 20% of the polymer melt velocity exiting the spinneret.

21. The process of 20, wherein said winding speed is no greater than 10% of the polymer melt velocity exiting the spinneret.

22. The process of 19, wherein said thermoplastic elastomer polymer is a thermoplastic polyurethane.

Claims

1. A melt spun elastic fiber comprising a polyester thermoplastic polyurethane (TPU) prepared from a reaction mixture comprising a polyisocyanate, a linear hydroxyl terminated polyester intermediate and one or more chain extenders, wherein the hydroxyl terminated polyester intermediate comprises the reaction product of

- an esterification reaction of one or more glycols with one or more dicarboxylic acids or anhydrides, or
- a transesterification reaction of one or more glycols with esters of dicarboxylic acids.

2. The fiber of claim 1, wherein the polyisocyanate is diphenyl methane-4,4' diisocyanate (MDI).

3. The fiber of claim 1, wherein the hydroxyl terminated polyester intermediate comprises the reaction product of adipic acid and a mixture of 1,4-butanediol (BDO) and 1,6-hexanediol (HDO).

4. The fiber of claim 1, wherein the chain extender is 1,4-butanediol (BDO).

5. The fiber of claim 1, wherein said fiber is crosslinked with a polyether crosslinking agent.

6. The fiber of claim 1, wherein said polyester thermoplastic polyurethane has a weight average molecular weight of from 200,000 to 700,000 Daltons.

7. The fiber of claim 5, wherein said crosslinking agent is from 5 to 20 weight percent of the combined weight of said polyester thermoplastic polyurethane and said crosslinking agent.

8. The fiber of claim 5, wherein said crosslinking agent is from 8 to 12 weight percent of the combined weight of said polyester thermoplastic polyurethane and said crosslinking agent.

9. A fabric comprising at least two different fibers wherein at least one of said fibers is the fiber of claim 1 and at least one of said fibers is a hard fiber.

10. The fabric of claim 9, wherein said fabric is made up of two strands of the fiber of claim 1 for every one strand of hard fiber.

11. The fabric of claim 9, wherein the fiber of claim 1 has a denier of from 20 to 600.

12. The fabric of claim 9, wherein said hard fiber is selected from the group consisting of Nylon and polyester.

13. The fabric of claim 12, wherein said hard fiber has a denier of about 70 and said thermoplastic polyurethane fiber has a denier of about 140.

14. An article of clothing comprising the fabric of claim 9.

15. The article of clothing of claim 14, wherein said article is an undergarment or a tight fitting garment.

FIG. 1

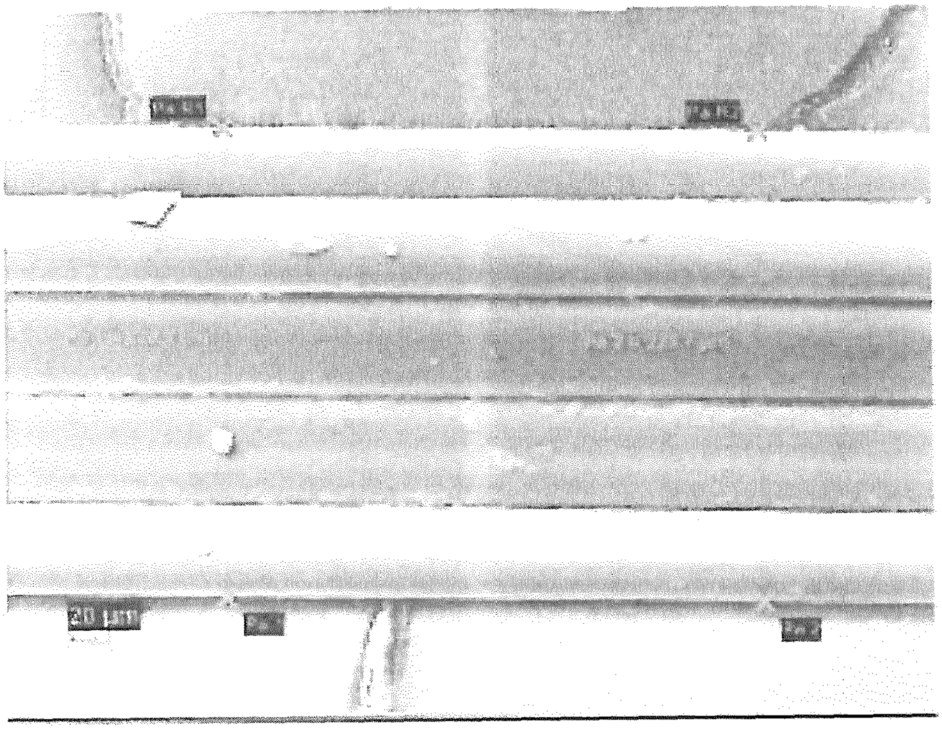


FIG. 2

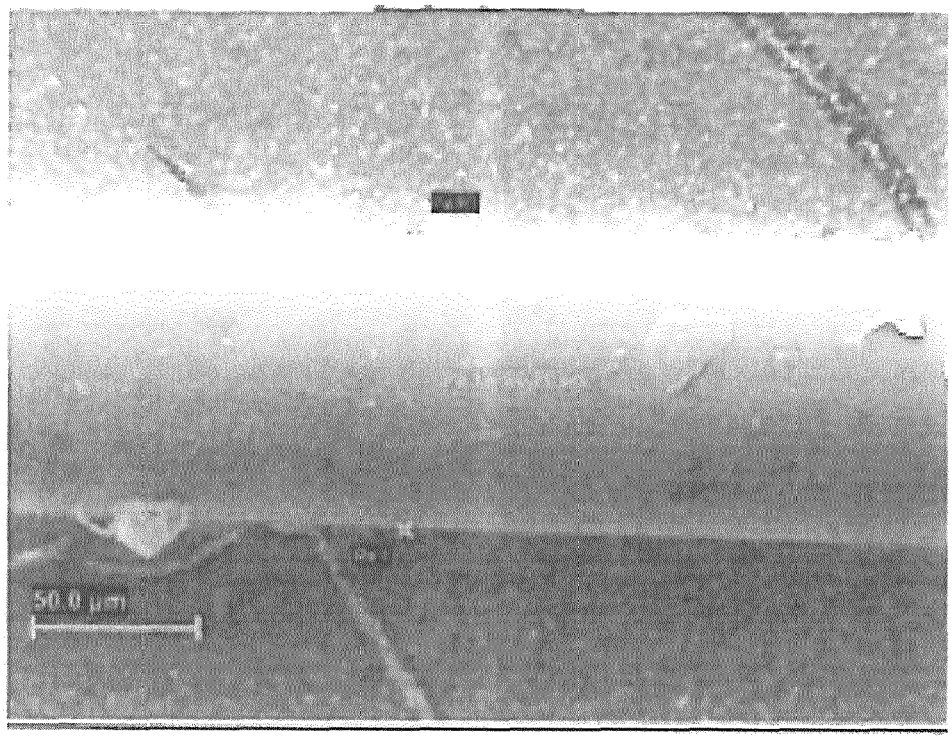
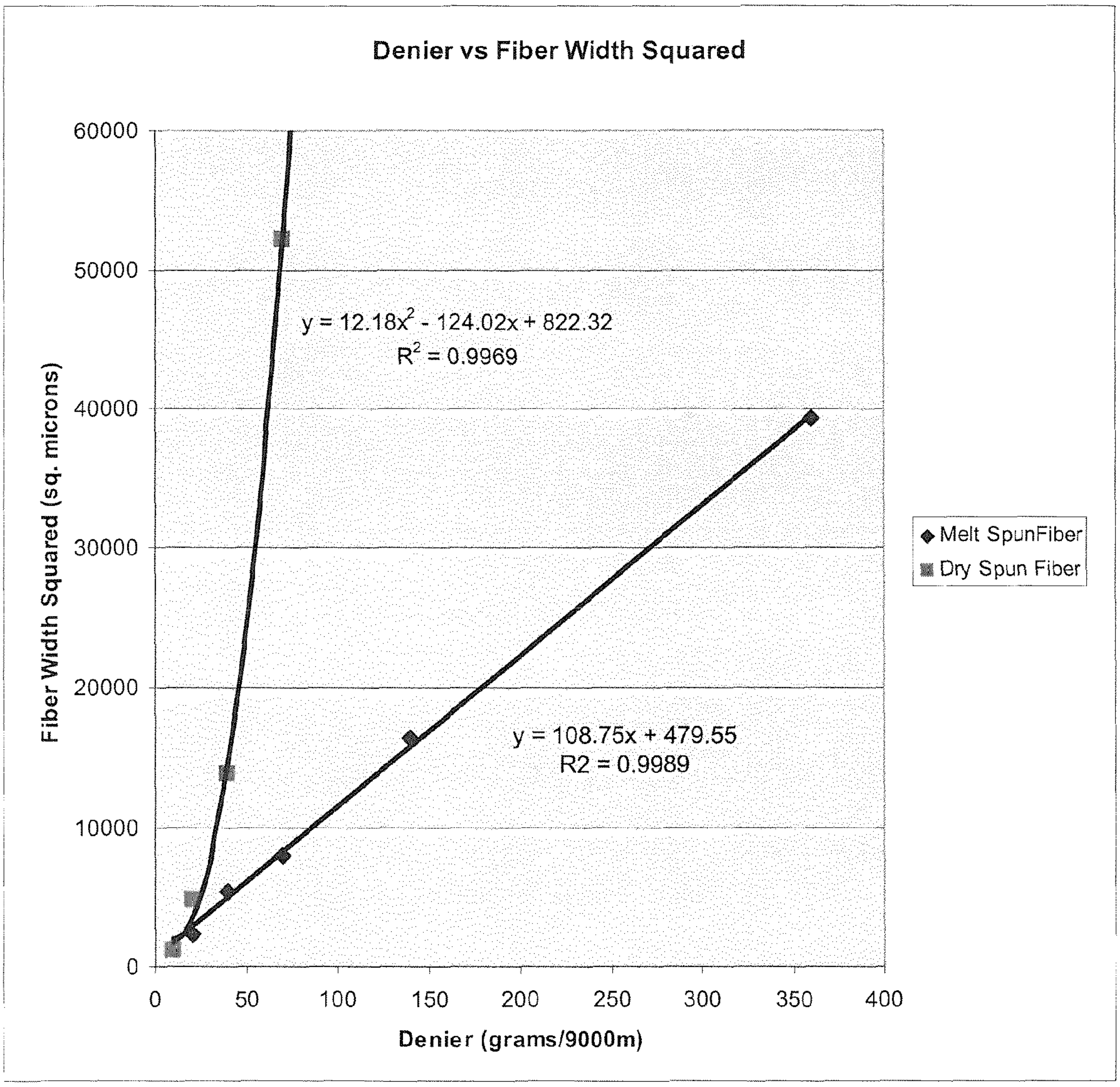


FIG. 3


Denier vs Fiber Width Squared
60000
50000
40000
30000
20000
10000
0
0
50
100
150
200
250
300
350
400
Fiber Width Squared (sq. microns)
Denier (grams/9000m)
y = 12.18x² - 124.02x + 822.32
R² = 0.9969
y = 108.75x + 479.55
R2 = 0.9989
◆ Melt SpunFiber
■ Dry Spun Fiber

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EUROPEAN SEARCH REPORT

Application Number
EP 13 15 5264

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X	US 2004/266301 A1 (VEDULA RAVI R [US] ET AL) 30 December 2004 (2004-12-30) * paragraphs [0037], [0047]; claims 20, 67; example 6 * -----	1-15	INV. D01D5/08 D01F6/00 D01F6/70
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			D01D D01F

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
Munich	1 March 2013	Lux, Rudolf

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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D : document cited in the application
L : document cited for other reasons
&. : member of the same patent family, corresponding document

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

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