

BICOMPONENT THERMOPLASTIC POLYURETHANE FIBERS AND FABRICS
MADE THEREFROM

TECHNICAL FIELD

[0001] The present technology relates to bicomponent fibers and fabrics made therefrom, in particular, core-sheath fibers, made from two different thermoplastic polyurethanes to provide a fiber having unique properties.

SUMMARY OF THE INVENTION

[0002] The present invention relates to a bicomponent fiber, wherein the bicomponent fiber has a core and sheath structure, wherein the bicomponent fiber comprises (a) a core comprising a first polyester thermoplastic polyurethane which has a melting enthalpy of at least 50 J/g measured according to ASTM D3418 and (b) a sheath comprising a second polyester thermoplastic polyurethane which has a melting enthalpy of 5 J/g or less measured according to ASTM D3418.

[0003] The present invention also relates to fabrics made from the bicomponent fibers of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0004] The term “bicomponent fiber” as used herein, refers to a conjugated product of at least two melt-spinnable components, wherein the conjugated product has at least two different longitudinally coextensive polymeric segments. In one embodiment, the bicomponent fiber of the present invention comprises two different polymer materials intimately adhered to each other along the length of the fiber, so that the fiber cross-section is for example, a core-sheath arrangement.

[0005] The bicomponent fiber of the present invention is made from two different polyester thermoplastic polyurethanes. A thermoplastic polyurethane is generally prepared by reacting a polyisocyanate with a polyol intermediate, and optionally a chain extender all of which are well known to those skilled in the art.

[0006] The bicomponent fiber of the present invention uses two different thermoplastic polyurethane materials, each based on a different polyester polyol intermediate. Hydroxyl terminated polyester intermediates are generally a linear polyesters 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. These polyester polyols 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. 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.

[0007] In one embodiment, the fiber of the present invention includes a first thermoplastic polyurethane based on the butanediol succinate and a second thermoplastic polyurethane based on butanediol adipate.

[0008] Thermoplastic polyurethanes used in the present invention are made using a polyisocyanate component. In some embodiments, the polyisocyanate component includes one or more diisocyanates. Useful polyisocyanates may be selected from aromatic polyisocyanates or aliphatic polyisocyanates or combinations thereof. Examples of useful polyisocyanates include, but are not limited to aromatic diisocyanates such as 4,4'-methylenebis(phenyl isocyanate) (MDI), *m*-xylene diisocyanate (XDI), phenylene-1,4-diisocyanate, 3,3'-dimethyl-4,4'-biphenylene diisocyanate (TODI), 1,5-naphthalene diisocyanate (NDI), and toluene diisocyanate (TDI), as well as aliphatic diisocyanates such as isophorone diisocyanate (IPDI), 1,6-

hexamethylene diisocyanate (HDI), 1,4-cyclohexyl diisocyanate (CHDI), decane-1,10-diisocyanate, lysine diisocyanate (LDI), 1,4-butane diisocyanate (BDI), and dicyclohexylmethane-4,4'-diisocyanate (H12MDI). In some embodiments, mixtures of two or more polyisocyanates may be used.

[0009] In some embodiments, the polyisocyanate component comprises or consists of one or more aromatic diisocyanates. In some embodiments, the polyisocyanate component is essentially free of, or even completely free of, aliphatic diisocyanates.

[0010] The thermoplastic polyurethane compositions described herein are optionally made using a chain extender component. Chain extenders include may include diols, diamines, and combination thereof.

[0011] Suitable chain extenders include relatively small polyhydroxy compounds, for example lower aliphatic or short chain glycols having from 2 to 20, or 2 to 12, or 2 to 10 carbon atoms. Suitable examples include ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, 1,4-butanediol (BDO), 1,6-hexanediol (HDO), 1,3-butanediol, 1,5-pentanediol, neopentylglycol, 1,4-cyclohexanedimethanol (CHDM), 2,2-bis[4-(2-hydroxyethoxy) phenyl]propane (HEPP), hexamethylenediol, heptanediol, nonanediol, dodecanediol, 3-methyl-1,5-pentanediol, ethylenediamine, butanediamine, hexamethylenediamine, and hydroxyethyl resorcinol (HER), and the like, as well as mixtures thereof.

[0012] The above three necessary ingredients (hydroxyl terminated intermediate, polyisocyanate, and chain extender) are preferably reacted in the presence of a catalyst.

[0013] 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.

[0014] The thermoplastic polyurethanes of this invention can be made by any of the conventional polymerization methods well known in the art and literature.

[0015] 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 molecular weight (Mw) of thermoplastic polyurethanes useful in the present invention may be from about 50,000 Daltons to about 300,000 Daltons, for example, 50,000 Daltons to about 100,000 Daltons as measured by GPC relative to polystyrene standards. In one embodiment, the thermoplastic polyurethane used for the sheath in the bicomponent fiber of the present invention has a molecular weight of about 50,000 Daltons to 75,000 Daltons. In one embodiment, the thermoplastic polyurethane used for the core in the bicomponent fiber of the present invention has a molecular weight of about 80,000 Daltons to about 100,000 Daltons.

[0016] 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. 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. 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.

[0017] 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, wollastonite, 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'-hydroxyphenyl) benzotriazoles and 2-hydroxybenzophenones.

[0018] Plasticizer additives can also be utilized advantageously to reduce hardness without affecting properties.

[0019] Bicomponent continuous filaments of the present invention can be made using a melt-spinning process. Figure 1 illustrates the typical bicomponent melt spinning technique with a pair of extruders. The steps for making the bicomponent fibers include vacuum batch drying at 80°C for 12 hours, feeding of dried thermoplastic polyurethane polymers into extruder from a hopper, melting the first and second thermoplastic polyurethane compositions in respective extruders with 1.24 inch single screw and an L/D of 24, and extruding the melts using two feeding systems/conduits by a melt pump and then to a spinneret or die. The back pressure at the extruder outlet was kept constant with a loop control. The extruder had four heating zones that were maintained between 180°C – 220°C. The basic system consists of two feeding systems, two polymers to the spin packs and a distribution system to meter both polymers to the die. It should be understood by those skilled in the art that the spinneret for producing bicomponent or multicomponent filaments is known in the industry. Such a process is described in US Patent No. 5,162,074, which is incorporated herein by reference. Typically, spinneret includes a casing containing spin packs, plurality of plates to create a pattern for polymer to flow. The bicomponent continuous filament spinnerets may also be configured for extrudate to have desired cross-sections such as symmetrical (concentric) core/sheath, asymmetrical core/sheath, side-by-side, crescent shaped and the like. Additionally, multiple extruders can be added to increase the number of components.

[0020] Once the fiber exits the spinneret, it is cooled before winding onto bobbins. The fiber is passed over a set of godets, finish oil is applied, and the fiber proceeds to another set of godets.

[0021] In some embodiments, during the melt spinning process, the thermoplastic polyurethane described above may be crosslinked with a crosslinking agent. Crosslinking agents are generally a pre-polymer of a hydroxyl terminated intermediate that is a polyether, polyester, polycarbonate, polycaprolactone, or mixture thereof reacted with a polyisocyanate. Crosslinking agents (also referred to as pre-polymers in some cases), often 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.

[0022] In one embodiment of the present invention, bicomponent fiber is formed without the use of crosslinking agents. In this embodiment, both the core thermoplastic polyurethane and the sheath thermoplastic polyurethane are free of crosslinking.

[0023] The bicomponent 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 bicomponent fibers of this invention are typically made in sizes ranging from, 20 to 2500 denier, for example 20 to 600 denier, further for example 40 to 400 denier.

[0024] When bicomponent 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.

[0025] A bicomponent fiber in accordance with the present invention has a core and sheath structure, wherein the bicomponent fiber has a core comprising a first polyester thermoplastic polyurethane, wherein the first polyester thermoplastic polyurethane has a melting enthalpy of at least about 50 J/g, for example, about 60 J/g, measured according to ASTM D3418 (DSC, second heat cycle) and a sheath comprising a second polyester thermoplastic polyurethane, wherein the second polyester thermoplastic polyurethane has a melting enthalpy of about 5 J/g or less measured according to ASTM D3418 (DSC, second heat cycle). In one embodiment of this bicomponent fiber, the first polyester thermoplastic polyurethane

has a contact clarity of 4% or less as measured according to ASTM D1003. In another embodiment of this bicomponent fiber, the second polyester thermoplastic polyurethane has a contact clarity of at least 12% measured according to ASTM D1003.

[0026] The bicomponent fiber of the present invention contains a core thermoplastic polyurethane and a sheath thermoplastic polyurethane, where the core and the sheath thermoplastic polyurethane materials are different from each other. In one embodiment, the core thermoplastic polyurethane comprises the reaction product of butanediol succinate and an aromatic diisocyanate while the sheath thermoplastic polyurethane comprises the reaction product of butanediol adipate, an aromatic diisocyanate, and at least one chain extender glycol.

[0027] In the present invention, the bicomponent fiber comprises about 10% to about 35% by weight of the core thermoplastic polyurethane composition and about 65% to about 90% by weight of the second thermoplastic polyurethane.

[0028] In one embodiment of the present invention, the final bicomponent fiber has low shrinkage and good clarity. For some applications, it is desired to have a bicomponent fiber having a shrinkage after 90 seconds of exposure at 70 °C of less than about 20% and a contact clarity measured according to ASTM D1003 of greater than about 13%. The present invention provides these properties surprisingly by combining two different thermoplastic polyurethane materials having different shrinkage and clarity properties. In one embodiment, the core comprises a thermoplastic polyurethane composition having a melting enthalpy of at least 50J/g measured according to ASTM D3418 and a contact clarity of about 4% or less as measured according to ASTM D1003 and the sheath comprises a thermoplastic polyurethane composition having a melting enthalpy of about 5 J/g or less measured according to ASTM D3418 (DSC, second heat cycle) and a contact clarity of at least 12% measured according to ASTM D1003. In another embodiment, the core thermoplastic polyurethane has a shrinkage of less than about 10% after 90 seconds exposure at 70 °C, while the sheath thermoplastic polyurethane has a shrinkage of about 40% to about 60% after 90 seconds exposure at 70 °C. Shrinkage is measured by using a one meter long length of the fiber and measuring it before and after exposure to the elevated temperature. The difference between the two measurements is the shrinkage.

[0029] The present invention also includes a fabric comprising the bicomponent fiber of the present invention. In one embodiment, the fabric comprises a bicomponent fiber, wherein the bicomponent fiber has a core and sheath structure, wherein the core comprises a thermoplastic polyurethane composition having a melting enthalpy of at least about 50 J/g, for example about 60 J/g, measured according to ASTM D3418 (DSC, second heat cycle) and a contact clarity of 4% or less as measured according to ASTM D1003 and the sheath comprises a thermoplastic polyurethane composition having a melting enthalpy of about 5 J/g or less measured according to ASTM D3418 (DSC, second heat cycle) and a contact clarity of at least about 12% measured according to ASTM D1003. In one embodiment, the core thermoplastic polyurethane composition has a shrinkage of less than about 10% after 90 seconds exposure at 70 °C and the sheath thermoplastic polyurethane composition has a shrinkage of about 40% to about 60% after 90 seconds exposure at 70 °C. In the fabric in accordance with the present invention, the bicomponent fiber comprises a core to sheath ratio of 10:90 to 35:65. 5.

[0030] In another embodiment, the fabric of the present invention comprises a bicomponent fiber that has a shrinkage after 90 seconds of exposure at 70 °C of less than about 20% and a contact clarity measured according to ASTM D1003 of greater than about 13%. The bicomponent fiber used in the fabric may also have a melting range of 100 °C to 120 °C measured by DSC.

[0031] Fabric made using the fibers of this invention can be made by knitting or weaving. In some embodiments, fabrics can be made by using the bicomponent fibers of the present invention with other fibers, such as nylon and/or polyester. The fabrics of the present invention may be used to make garments, such as for sports apparel applications. The enhanced clarity of the fibers of the present invention also provides benefits for applications where graphics are applied to the fabrics.

[0032] The invention will be better understood by reference to the following examples.

[0033] Filaments were prepared based on the thermoplastic polyurethanes listed in Table 1. TPU 1 is a polyester thermoplastic polyurethane comprising the reaction product of butanediol succinate and an aromatic diisocyanate having a melt enthalpy measured by DSC, second heat cycle of 60 J/g. TPU 2 is a polyester thermoplastic polyurethane comprising the reaction product of butanediol adipate, an aromatic diisocyanate, and a chain extender diol

having a melt enthalpy measured by DSC, second heat cycle of 5 J/g. Comparative Examples C1 – C9 were made from either 100% of one TPU material or blends of pellets of TPU 1 and TPU 2 to form a mono-component filament. Inventive Examples 1-4 are bicomponent fibers having a core-sheath cross section. When fibers were able to be successfully made, these were tested for shrinkage using a one meter length of fiber that was measured before and after exposure to a temperature of 70 °C for 90 seconds.

Table 1

Example	TPI 1 (wt %)	TPU 2 (wt %)	Shrinkage (%)	Clarity (%) ASTM D1003	Comments
C1		100	40	12	Too high shrinkage
C2	100		4	4	Very opaque
C3	10	90	45-60	NA	Shrinking after fusing ¹
C4	25	75	45		Shrinking after fusing ¹
C5	35	65			Filament breaks during spinning ²
C6	50	50			Filament breaks during spinning ²
C7	65	35			Filament breaks during spinning ²
C8	75	25			Filament breaks during spinning ²
C9	90	10			Filament breaks during spinning ²
Inv 1	75	25	10	5	
Inv 3	40	60	11	7	
Inv 4	25	75	13	13	

¹ Filaments were spun and knitted into a fabric. Heat was applied to fuse the fibers in the fabric. The fabric shrunk and deformed such that a clarity measurement could not be obtained.

² A continuous filament could not be made with these blends. Incompatibility (immiscibility non-miscibility) between the two TPU materials caused the blend to have insufficient melt strength to make a continuous filament.

[0034] As shown by the data above, blends of two incompatible thermoplastic polyurethanes could not form a continuous filament with both acceptable shrinkage and clarity. However, bicomponent fibers of the same two thermoplastic polyurethane compositions unexpectedly provided both high clarity and low shrinkage.

[0035] Except in the Examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials, reaction conditions, molecular weights, number of carbon atoms, and the like, are to be understood as modified by the word “about.” It is to be understood that the upper and lower amount, range, and ratio limits set forth herein may be independently combined. Similarly, the ranges and amounts for each element of the invention can be used together with ranges or amounts for any of the other elements.

[0036] As used herein, the transitional term “comprising,” which is synonymous with “including,” “containing,” or “characterized by,” is inclusive or open-ended and does not exclude additional, un-recited elements or method steps. However, in each recitation of “comprising” herein, it is intended that the term also encompass, as alternative embodiments, the phrases “consisting essentially of” and “consisting of,” where “consisting of” excludes any element or step not specified and “consisting essentially of” permits the inclusion of additional un-recited elements or steps that do not materially affect the essential or basic and novel characteristics of the composition or method under consideration.

[0037] While certain representative embodiments and details have been shown for the purpose of illustrating the subject invention, it will be apparent to those skilled in this art that various changes and modifications can be made therein without departing from the scope of the subject invention. In this regard, the scope of the invention is to be limited only by the following claims.