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(54) **CONDUCTIVE SOIL-REPELLENT CORE-SHEATH FIBER OF HIGH CHEMICAL RESISTANCE, ITS PREPARATION AND USE**

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(57) **ABSTRACT**

Conductive soil-repellent core-sheath fiber of high chemical resistance, its preparation and use

Described is a melt-spun fiber having a core-sheath structure and a high tensile strength whose core contains a synthetic thermoplastic polymer which is not a fluoropolymer and whose sheath contains at least one melt-spinnable fluoropolymer and particles comprising electroconductive material.

The fibers of the invention are useful especially in the form of monofilaments for producing textile fabrics for industrial applications

CONDUCTIVE SOIL-REPELLENT CORE-SHEATH FIBER OF HIGH CHEMICAL RESISTANCE, ITS PREPARATION AND USE

[0001] The present invention relates to conductive soil-repellent core-sheath fibers, especially monofilaments, which are useful in industrial fabrics in particular.

[0002] It is known that fluoropolymers have good thermal stability, good chemical resistance and soil-repellent properties. It has already been attempted to process melt-spinnable fluoropolymers into fibers, multi- and monofilaments in order that textile fabrics for industrial applications that have the abovementioned properties of fluoropolymers may be manufactured therefrom. The disadvantage with melt-spinnable fluoropolymers is the high creep. Fibers and filaments formed from this material therefore have only low tensile strengths and are not shape stable.

[0003] It has also already been tried to combine fluoropolymers with polymers having good mechanical performance characteristics, for example with polyethylene terephthalate (hereinafter also referred to as PET). However, it is to be noted in this context that fluoropolymers are often incompatible with other polymers in that they generally do not mix with them. The result is thus frequently a two-phase mixture in which the fluoropolymers form three-dimensional islands. The weight fraction of fluoropolymer which can be added is thus frequently limited, since the boundary layers of the polymers have only poor adhesion to each other. This property manifests itself in fibers as a tendency to split.

[0004] Monofilaments composed of PET and random copolymers of ethylene and tetrafluoroethylene (ETFE) have been commercially available for years. Frequently, these fibers have a low carboxyl end group content to stabilize them against hydrolysis and are stabilized with carbodiimides to cap the carboxyl end groups. The capping of carboxyl groups by means of carbodiimides is described for example in EP-A417,717 and EP-A-503,421.

[0005] Industrial fabrics woven from these monofilaments do largely have the mechanical properties of a PET filament, but combined with increased hydrolysis resistance and improved soil repellency.

[0006] Because the fluoropolymer fraction is relatively low, the thermal stability and chemical resistance of these fibers are substantially equal to the data for pure PET. However, the increased tendency to split can manifest itself under mechanical stresses, for example at the beating up of the fell on the weaving machine.

[0007] Fibers composed of synthetic polymers and woven fabrics produced therefrom have the disadvantage, however, that they can become charged up with static electricity as a result of friction. Conductive fibers for producing textile fabrics, such as wovens for industrial use, or for other applications, for example brushes, have long been the goal of numerous developments.

[0008] DE-A-1 98 26 120 discloses a flame-retardant electroconductive woven fabric which contains electroconductive and flameproofed nonelectroconductive fibers. The electroconductive fibers can contain electroconductive particles, such as carbon black or metal particles, be coated with metal or consist of electroconductive materials, such as polyanilines. The fiber materials mentioned are polyester and polyolefins.

[0009] DE-U-86 238 79 discloses yarn for the manufacture of spiral tapes which is sheathed with a layer of curable polymer. This layer contains electroconductive carbon. Melamine resins, epoxides, phenolic resins or polyurethanes are mentioned by way of example as polymers for the sheath layer.

[0010] DE-A-39 38 414 describes high-strength woven fabric which is formed from artificial fibers, these being incorporated in the form of electroconductive fibers in the warp and the weft, and which contains nonelectroconductive fibers as well. The electroconductive fibers consist of polyolefins and contain graphite or carbon black.

[0011] EP-A-160,320 describes hairbrush core-sheath monofilaments composed of selected polymers. The core contains nylon or polyesters which comprise at least 60% by weight of polybutylene terephthalate units. The sheath contains specific nylon grades or copolyetherester.

[0012] DE-U-86/06334 discloses core-sheath fibers whose core consists of thermoplastic polymer, preferably of polyamide, and whose sheath consists of electroconductive polymer, preferably of polyamide, which contains embedded carbon black or metals.

[0013] JP-A-07/278,956 describes electroconductive copolyesters which mainly contain polybutylene terephthalate units and which are doped with carbon black. It also describes core-sheath fibers composed of this material which have a core which consists of aromatic polyester.

[0014] WO-A-98/14,647 discloses electroconductive heterofilaments which can be configured as core-sheath fibers for example. Examples described of core and sheath polymers are PET and other polyesters or PET/nylon.

[0015] WO-A-01/20,076 discloses nonwovens having a high dielectric constant. Mixtures of polyvinylidene fluoride and polypropylene are proposed as fiber material. The products formed therefrom are notable for a long half-life for electrostatic charges and can be used as electrostatic filters.

[0016] U.S. Pat. No. 6,085,061 describes a brush for cleaning electrostatically charged surfaces. The fiber materials used can be core-sheath fibers whose core is electroconductive and whose sheath consists of polyvinylidene fluoride.

[0017] DE-A44 12 396 discloses melt-spun undrawn nonelectroconductive fibers having a core-sheath structure whose sheath contains fluoropolymers. The core polymer used is polycarbonate. This fiber is used as an optical fiber and is unsuitable for industrial textiles, such as industrial wovens for example, on account of its low strengths. Moreover, the critical properties with an optical fiber are high reflection at the boundary layer and very low attenuation of the electromagnetic wave. Both these properties can only be achieved through use of a high-purity coating.

[0018] JP-A-2001-127,218 describes a semiconducting fiber composed of a fluoropolymer which contains carbon black. This fiber does not have a core-sheath structure and is used for manufacturing nonwovens, for example by the melt-blow process. The fiber has not been drawn.

[0019] It is an object of the present invention to combine the performance advantages of the materials known for fiber production without having to incur the disadvantages associated with the use of the individual materials.

[0020] A person skilled in the art knows that bonding problems are normal at the boundary layer between two polymers. This holds especially for the use of known poor-bonding fluoropolymers with other polymers. It has been determined that, surprisingly, the use of a fluoropolymer which is doped with electroconductive particles provides very good bonding to the polymer core.

[0021] It is thus a further object of the present invention to provide core-sheath fibers which possess good bonding between the individual layers.

[0022] The present invention thus provides fibers, especially monofilaments, which combine antistatic properties with high chemical and thermal stability and good mechanical shape stability and also high tensile strength.

[0023] This invention is a melt-spun fiber having a core-sheath structure and a tensile strength of at least 15 cN/tex whose core contains a synthetic thermoplastic polymer which is not a fluoropolymer and whose sheath contains at least one melt-spinnable fluoropolymer and particles comprising electroconductive material.

[0024] The synthetic thermoplastic polymers forming the core are freely chooseable, as long as they are melt spinnable and provide the fiber with the properties desired for the particular intended application. Fluoropolymers are not comprehended by synthetic thermoplastic polymers, even though the core may contain fluoropolymers as a blend component as well as synthetic thermoplastic polymers.

[0025] Examples of synthetic thermoplastic materials are polyolefins, such as polyethylene, polypropylene or copolymers containing ethylene and/or propylene units combined with other copolymerized alpha-olefin units, such as alpha-butylene, alpha-pentylene, alpha-hexylene or alpha-octylene; polyesters, such as polycarbonate, aliphatically aromatic polyesters or wholly aromatic polyesters; polyamides, such as aliphatic or aliphatically aromatic polyamides (nylons) or wholly aromatic polyamides (aramids); or polyether ketones, ie polymers which have at least ether and ketone groups and generally aromatic divalent radicals, such as phenylene, in the recurring chain, many combinations of these groups being possible, for example PEK, PEEK or PEKK; or polyarylene sulfides, preferably polyphenylene sulfide; or polyether esters, ie polymers which have at least ether and ester groups and generally aromatic divalent radicals, such as phenylene, in the recurring chain, for example TPE-E; or polyacrylonitrile or polyacrylonitrile copolymers with other ethylenically unsaturated comonomers, such as acrylic or methacrylic acid.

[0026] Preferably, the core of the core-sheath fibers of this invention contains polyamides and especially polyesters.

[0027] The thermoplastic polyamides which are preferably used in the compositions of the present invention are known per se.

[0028] Examples thereof are fiber-forming polyamides, such as aliphatic or aliphatically aromatic polyamides, for example polycaprolactam, poly(hexamethylene-1,6-diamineadipamide), poly(hexamethylene-1,6-diaminesebacamide), poly(hexamethylene-1,6-diamineterephthalamide) or poly(hexamethylene-1,6-diamineisophthalamide); or else wholly aromatic polyamides, such as poly(phenylene-1,4-diamineterephthalamide) or poly(phenylene-1,4-diamineisophthalamide).

[0029] The polyamides used in this invention have DIN 53727 viscosity numbers which are customarily in the range from 120 to 350 and preferably from 150 to 320 cm^3/g (measured at 25° C. in sulfuric acid).

[0030] The thermoplastic polyesters and/or aromatic liquid-crystalline polyesters which are more preferably used in the compositions of the present invention are known per se.

[0031] Examples thereof are fiber-forming polyesters, such as polycarbonate or aliphatically aromatic polyesters, for example polybutylene terephthalate, polycyclohexanedimethyl terephthalate, polyethylene naphthalate or especially polyethylene terephthalate, or else wholly aromatic, liquid-crystalline polyesters, such as polyoxybenzonaphthoate. Building blocks of fiber-forming polyesters are preferably diols and dicarboxylic acids or appropriately constructed hydroxy carboxylic acids. The main acid constituent of the polyesters is terephthalic acid or cyclohexanedicarboxylic acid, but other aromatic and/or aliphatic or cycloaliphatic dicarboxylic acids may be suitable as well, preferably para- or trans-disposed aromatic compounds, such as for example 2,6-naphthalenedicarboxylic acid or 4,4'-biphenyldicarboxylic acid, or else p-hydroxybenzoic acid. Aliphatic dicarboxylic acids, such as adipic acid or sebacic acid for example, are preferably used in combination with aromatic dicarboxylic acids.

[0032] Typical suitable dihydric alcohols are aliphatic and/or cycloaliphatic and/or aromatic diols, for example ethylene glycol, propanediol, 1,4-butanediol, 1,4-cyclohexanedimethanol or else hydroquinone. Preference is given to aliphatic diols which have 2 to 4 carbon atoms, especially ethylene glycol; preference is further given to cycloaliphatic diols, such as 1,4-cyclohexanedimethanol.

[0033] Preferred thermoplastic polyesters are especially selected from the group consisting of polyethylene terephthalate, polyethylene naphthalate, polybutylene naphthalate, polypropylene terephthalate, polybutylene terephthalate, polycyclohexanedimethanol terephthalate, polycarbonate or a copolycondensate containing polybutylene glycol, terephthalic acid and naphthalenedicarboxylic acid units.

[0034] Further preferred thermoplastic polyesters are aromatic, liquid-crystalline polyesters, especially polyesters containing p-hydroxybenzoate units.

[0035] Especially in the case of fibers which are to be used in hot moist environments, such as monofilaments for use in paper machines, and which contain polyesters as a core component, these polyesters are preferably stabilized against hydrolytic degradation by addition of polyester stabilizers.

[0036] Such stabilized fibers exhibit a significant reduction in the degradation tendency of the polyester, so that monofilament lifetimes can be achieved which are equivalent to those of monofilaments based on extremely stable fiber materials, such as polyarylene sulfides or oxides.

[0037] Particular preference is given to fibers containing stabilized polyesters and particularly preferably carbodiimides in the core.

[0038] The polyesters used in the present invention typically have solution viscosities (IV values) of at least 0.60 dl/g, preferably of 0.60 to 1.05 dl/g, more preferably of 0.62-0.93 dl/g, (measured at 25° C. in dichloroacetic acid).

[0039] The fluoropolymers forming the sheath are likewise freely chooseable, as long as they are melt spinnable.

[0040] The fluoropolymers used in the present invention are poly(fluoroolefin) homopolymers and/or copolymers derived from ethylenically unsaturated fluorous olefin monomers and other monomers which are copolymerizable therewith. Such polymers are likewise known per se.

[0041] Examples thereof are melt-spinnable copolymers of tetrafluoroethylene with other alpha-olefins, such as ethylene, propylene, butylene, hexylene or octylene.

[0042] But it is also possible to use homo- or copolymers which are derived from other fluorous monomers, for example from mono-, di-, trifluoroethylene, from vinyl fluoride or especially from vinylidene fluoride.

[0043] Particular preference is given to using melt-spinnable copolymers of tetrafluoroethylene with at least one alpha-olefin, preferably with ethylene.

[0044] Very particular preference is given to using polyvinylidene fluoride (PVDF) as a sheath component.

[0045] When spinning polyesters, especially PET, with PVDF to form a bicomponent monofilament in a core-sheath structure there is a surprise in that very good core-sheath bonding is obtained.

[0046] The invention therefore also includes a heterofilament fiber containing at least two components, the first component being an electric insulator and comprising a thermoplastic polymer which is not a fluoropolymer and the second component comprising polyvinylidene fluoride.

[0047] The particles composed of electroconductive material which are present in the sheath of the melt-spun fiber of the present invention are freely chooseable, as long as they provide the sheath with an increased electroconductivity.

[0048] The particles can be composed of carbon, being for example carbon fibers, carbon black or graphite; of metals, for example of copper, silver, aluminum or iron; of metal alloys, for example bronze; or of conductive plastics, for example of polyanilines or of polypyrrole.

[0049] The particles can be present in any desired form, for example in fiber form or in the form of round or irregular particles.

[0050] The level of electroconductive particles in the sheath is to be chosen such that a distinct increase in the electroconductivity of the polymeric material results. Typical amounts vary in the range of up to 50% by weight and preferably 2 to 15% by weight, based on the amount of the sheath material.

[0051] Particular preference is given to melt-spun fibers wherein the sheath contains between 2% by weight and 15% by weight and especially between 4% by weight and 9% by weight of electroconductive particles.

[0052] The core-sheath fibers of the present invention can be present in any desired form, for example as multifilaments, as staple fibers or especially as monofilaments.

[0053] The linear density of the core-sheath fibers of the present invention can likewise vary within wide limits. Examples thereof are 100 to 45,000 dtex and especially 400 to 7,000 dtex.

[0054] Particular preference is given to monofilaments.

[0055] Particular preference is given to monofilaments whose cross-sectional shape is round, oval or n-gonal, where n is not less than 3.

[0056] The staple lengths in the case of staple fibers can likewise vary within wide limits, for example between 30 to 70 mm.

[0057] The core of the core-sheath fiber of the present invention forms the mechanical, load-bearing component of the fiber, whereas the sheath determines mainly the performance characteristics, such as antistatic performance and lubricity. The core can preferably utilize a commercially available PET raw material.

[0058] The sheath more preferably utilizes a fluoropolymer based on PVDF which was previously processed with carbon black in particular into a spinnable mixture.

[0059] The weight fraction of the core-forming component A) to the sheath-forming component B) is, based on the total amount of these components, 50 to 95% by weight and preferably 60 to 80% by weight for component A) and 50 to 5% by weight and preferably 40 to 20% by weight for component B).

[0060] The core-sheath fibers of the present invention can be prepared according to processes known per se.

[0061] These processes comprise the measures of:

[0062] i) selecting a first polymer which is a synthetic thermoplastic polymer and not a fluoropolymer and which has a first melting point,

[0063] ii) selecting a second polymer which contains particles comprising electroconductive material and which is a melt-spinnable fluoropolymer which has a second melting point at least 20° C. below the first melting point,

[0064] iii) coextruding the first polymer and the second polymer through a heterofilament spinneret at a spinning temperature above the first melting point to form a bicomponent fiber having a core comprising the first polymer and a sheath comprising the second polymer and

[0065] iv) drawing the produced core-sheath filament to increase the tensile strength.

[0066] The two polymers or mixtures containing these polymers are preferably dried directly before being fed into the extruder, melted in the extruder and filtered through a spin pack. The fluoropolymer is provided with the electroconductive particles. This is typically accomplished before the fluoropolymer is fed to the extruder, but can also take place directly upstream of the spin pack. It is similarly possible to use masterbatches containing the fluoropolymer and electroconductive particles.

[0067] After the polymer melts have been pressed through a heterofilament spinneret, the molten polymer thread is quenched in a spin bath, for example a water bath, and subsequently wound up or taken off. The takeoff speed is greater than the ejection speed of the polymer melt and thus causes stretching or drawing of the extruded thread.

[0068] The as-spun heterofilament thread thus produced is subsequently preferably subjected to an afterdrawing operation, more preferably in plural stages, especially to a two- or three-stage afterdrawing operation, to an overall draw ratio of 1:3 to 1:8 and preferably 1:4 to 1:6.

[0069] Drawing is preferably followed by heat setting, for which temperatures of 130 to 280° C. are employed; the length is maintained constant or shrinkage of up to 30% is allowed.

[0070] It has been determined to be particularly advantageous for the monofilaments of the present invention to operate at a melt temperature in the range from 285 to 315° C. and at a jet stretch ratio of 1:2 to 1:6.

[0071] The spinning takeoff speed is customarily 10-40 m per minute.

[0072] When the thermoplastic polymer of the core and the fluoropolymer of the sheath are spun into a bicomponent monofilament in core-sheath structure there is a surprise in that very good core-sheath bonding is obtained.

[0073] The conductivity of the sheath can be lost at drawing, but can be restored by a heat treatment and the thereby induced shrinkage, preferably above the melting point of the sheath material but below the melting temperature of the core.

[0074] The conductively doped fluoropolymer determines mainly the surface properties. The fibers of the present invention are notable for very good soil repellency, good chemical resistance and electroconductivity.

[0075] The combination with the fluoropolymer leads to fibers having improved lubricity properties compared with fibers composed of straight thermoplastic polymer. These fibers exhibit enhanced soil repellency compared with fibers composed of straight thermoplastic polymer.

[0076] The fibers of the present invention can contain assistants as well as components A) and B). Examples of assistants are processing assistants, stabilizers, antioxidants, plasticizers, lubricants, pigments, delusterants, viscosity modifiers or crystallization accelerants.

[0077] Examples of processing assistants are siloxanes, waxes or long-chain carboxylic acids or their salts, aliphatic, aromatic esters or ethers.

[0078] Examples of stabilizers and antioxidants are the abovementioned polyester stabilizers, phosphorus compounds, such as phosphoric esters or carbodiimides.

[0079] Examples of pigments or delusterants are organic dye pigments or titanium dioxide.

[0080] Examples of viscosity modifiers are polybasic carboxylic acids and their esters or polyhydric alcohols.

[0081] The fibers of the present invention, especially the monofilaments, are preferably used for producing textile fabrics, such as wovens, formed-loop knits, drawn-loop knits, non crimp fabrics and nonwovens.

[0082] Textile fabrics containing monofilaments of the present invention are especially useful for industrial applications, as for filters, as screen printing materials or especially as paper machine wires.

[0083] The monofilaments of the present invention have good textile-physical properties and are easy to process by weaving. The wovens have the usual shape stability of the thermoplastic polymers which form the core.

[0084] Wovens formed from these monofilaments are very useful for industrial cloths, especially in the filtration of aggressive media where there is also a risk of an electrostatic charge buildup; that is, especially in solid-gaseous and solid-liquid filtration.

[0085] The invention also includes the use of the fibers for producing textile fabrics which are used in environments featuring severe chemical and/or physical stress, especially as paper machine wires or industrial wovens, as for example in filtration, for producing conveyor belts or as reinforcing plies. Here the fibers are used as monofilaments and especially as weft threads in the woven fabric.

[0086] The use of the monofilaments of the present invention as paper machine wires can take place in the forming section, the pressing section or in particular the drying section. When used in the drying section, the monofilaments of the present invention are used as spiral wires in particular.

[0087] For these applications, the fibers used according to the present invention, especially in the form of monofilaments, typically have a linear density range from 10 to 4,500 tex, an elasticity modulus of 2.0 to 8.0 N/tex, a tenacity of 15 to 50 cN/tex, a breaking extension of 15 to 45% and a 180° C. hot air shrinkage of 1.0 to 20.0%.

[0088] The example which follows illustrates the invention without limiting it.

[0089] Core-sheath fibers composed of polyethylene terephthalate and polyvinylidene fluoride containing carbon black.

[0090] Polyethylene terephthalate (PET) (70% by weight) and polyvinylidene fluoride (as a masterbatch containing 9% by weight of conductivity carbon black; Palmarole EXP 184/14; 30% by weight) were melted in two extruders featuring separate temperature control (PET at 282° C. melting temperature (core material) and PVDF at 240° C. melting temperature (sheath material) and spun through a 20 hole spinneret having a hole diameter of 1.40 mm and a hauloff speed of 15 m/min to form a core-sheath monofilament, doubly drawn (first drawing in water bath at 80° C.; second drawing in hot air duct at 150° C.) and also heat set in the hot air duct at 205° C. The overall draw ratio was 4.1:1. The final diameter of the core-sheath monofilament was 0.500 mm.

[0091] The core-sheath monofilament obtained had the following properties:

Linear density:	2890 dtex
Tenacity:	24 cN/tex

-continued

160° C. hot air shrinkage 10':	2.5%
Loop tenacity:	>20 cN/tex
Breaking extension:	44%
12 cN/tex EASL:	8.5%
15 cN/tex EASL:	13%
El. resistance (10 mm clamped length):	$8 * 10^5$ (ohm)
El. resistance (150 mm clamped length):	$9 * 10^6$ (ohm)

What is claimed is:

1. A melt-spun fiber having a core-sheath structure and a tensile strength of at least 15 cN/tex whose core contains a synthetic thermoplastic polymer which is not a fluoropolymer and whose sheath contains at least one melt-spinnable fluoropolymer and particles comprising electroconductive material.

2. The melt-spun fiber of claim 1, wherein the synthetic thermoplastic polymer of the core is a polyamide and especially a polyester.

3. The melt-spun fiber of claim 2, wherein the polyester is a polyethylene terephthalate.

4. The melt-spun fiber of claim 2, wherein the polyester is a liquid-crystalline polyester.

5. The melt-spun fiber of claim 1, wherein the melt-spinnable fluoropolymer is a copolymer of tetrafluoroethylene with at least one alpha-olefin, preferably ethylene.

6. The melt-spun fiber of claim 1, wherein the melt-spinnable fluoropolymer is a polyvinylidene fluoride.

7. The melt-spun fiber of claim 1, wherein the sheath contains up to 50% by weight and preferably 2 to 15% by weight of electroconductive particles.

8. The melt-spun fiber of claim 6, wherein the sheath contains between 2% by weight and 15% by weight and especially between 4% by weight and 9% by weight of electroconductive particles.

9. The melt-spun fiber of claim 1, wherein the particles comprising electroconductive material consist of carbon, metals or metal alloys and are especially carbon black or graphite.

10. The melt-spun fiber of claim 1 which is a filament, especially a monofilament.

11. A process for preparing the melt-spun core-sheath fiber of claim 1, comprising the measures of:

i) selecting a first polymer which is a synthetic thermoplastic polymer and not a fluoropolymer and which has a first melting point,

ii) selecting a second polymer which contains particles comprising electroconductive material and which is a melt-spinnable fluoropolymer which has a second melting point at least 20° C. below the first melting point,

iii) coextruding the first polymer and the second polymer through a heterofilament spinneret at a spinning temperature above the first melting point to form a bicomponent fiber having a core comprising the first polymer and a sheath comprising the second polymer and

iv) drawing the produced core-sheath filament to increase the tensile strength.

12. The use of melt-spun core-sheath fibers of claim 1 for producing industrial wovens.

13. The use of claim 12, wherein the industrial woven is a paper machine wire, a filter cloth, a screen printing cloth, a conveyor belt or a reinforcing ply.

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