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(54) **COOLING FABRIC CONTAINING HYDROPHOBIC PEBA**

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(57) **ABSTRACT**

A hydrophobic polyether-block-polyamide copolymer (PEBA) for the manufacture of a fabric material capable of cooling after the material has been brought into contact with an aqueous medium at a temperature lying in the range from 15° C. to T_m-20° C., T_m being the melting point of the fabric material, the aqueous medium comprising at least 85 wt % water relative to the weight of the aqueous medium, the PEBA comprising 20 to 80 wt % polyamide blocks and 80 to 20 wt % polyether blocks and having a saturated water absorption of less than 6 wt % according to the ISO 62 standard relative to the weight of PEBA, a cooling fabric comprising such a PEBA and the use of this fabric in the medical, hygiene, baggage, confection, clothing, domestic or household equipment, furnishing, carpet, automotive or industrial fields, especially for industrial filtration, agricultural and/or building matter.

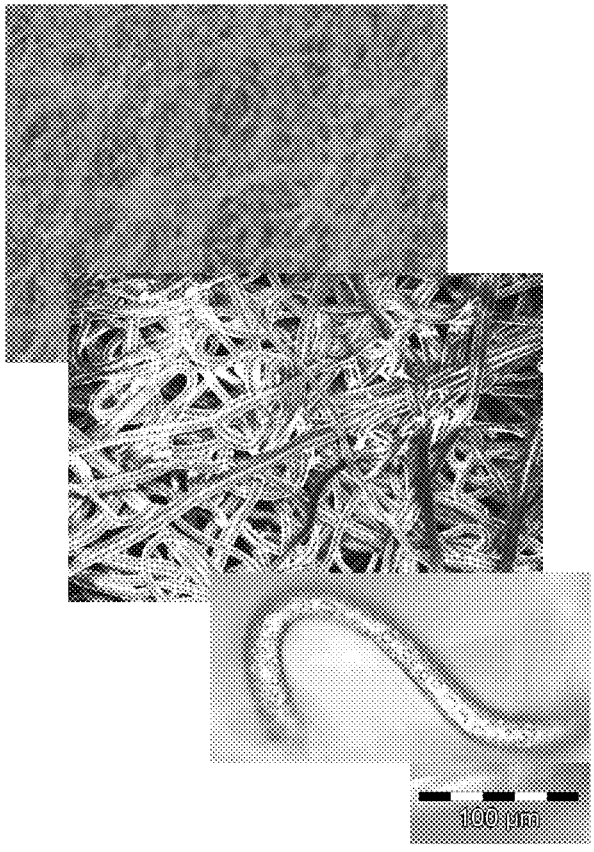
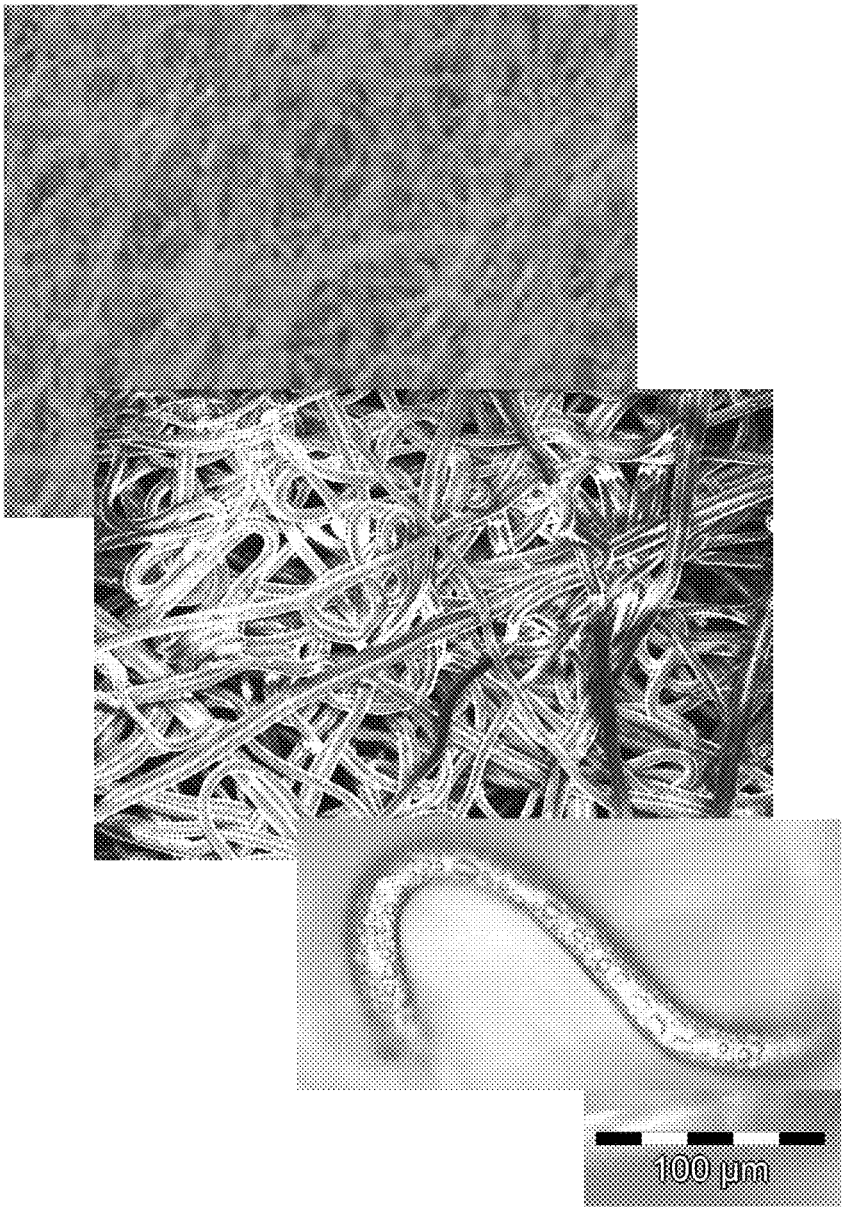


Figure 1



COOLING FABRIC CONTAINING HYDROPHOBIC PEBA

FIELD OF THE INVENTION

[0001] One subject of the present invention is a cooling fabric material comprising synthetic fibers made of a thermoplastic elastomer polymer.

[0002] In the present description of the invention:

[0003] The term "fabric material" or "fabric" is understood to mean any material made from fibers or filaments and any material forming a porous membrane characterized by a length/thickness ratio of at least 300;

[0004] The term "fiber" is understood to mean any synthetic or natural material characterized by a length/diameter ratio of at least 300; and

[0005] The term "filament" is understood to mean any fiber of infinite length. Found among fabrics are in particular: fibrous mats (for bandages, filters, felt); rovings (for bandages); yarns (for stitching, knitting or weaving); nonwovens; webs; nets; knits (straight, circular, fully-fashioned knits); wovens (traditional, jacquard, multiple, two-sides, multi-axial, 2.5D, 3D wovens) and many others.

PRIOR ART

[0006] The synthetic fibers made of thermoplastic polymer currently used to manufacture cooling fabrics have several drawbacks: they have a tendency to swell when impregnated with an aqueous medium, and their cooling capability is neither sufficiently intense nor durable. It is therefore necessary to modify these fibers or the fabrics obtained from these fibers so that they acquire a detectable or sufficient cooling capability. The processes used consist either in carrying out a chemical treatment of the surface of the fabric or, more commonly, in adding an absorbent polymer to the matrix of fibers. This absorbent polymer has the capability of increasing its volume by absorbing water so as to form a gel that provides a cooling effect by natural evaporation of the water, after which the gel resumes its initial volume. The cold produced is a "wet" cold, providing an uncomfortable or even sticky "wetted" sensation. Absorbent agents currently used are for example polyacrylate crystals, especially crosslinked sodium polyacrylate crystals. In addition, the level of stability of these cooling agents is not guaranteed. They may be seen to become denatured at temperatures above 100° C., or even sometimes above temperatures of around 40 or 60° C. Fabrics containing these agents must not be machine-washed, but hand-washed, nor can they be washed with detergents, nor can they be frozen.

[0007] In addition, these current techniques have several drawbacks. They require at least one additional production step to treat the surface and/or to add into the bulk an absorbent additive or polymer.

[0008] The object of the present invention is to provide cooling fabric materials having an intense and durable cooling effect, which have a sufficient level of stability with respect to water (they do not swell on contact with water) and with respect to temperature (they may withstand ambient temperature of around −60° C. to 150° C., preferably −40° C. to 140° C.

[0009] The object of the present invention is in particular to provide a simple process for manufacturing such fabric materials, which comprises the fewest possible steps, which does not impair the dimensional stability nor the flexibility of the fabric materials, nor their softness, and which preferably used bioresource raw materials.

[0010] Surprisingly, the applicant has found that the use of a particular polyether-block-polyamide copolymer makes it possible to manufacture such fabric materials with a remarkable cooling capability.

SUMMARY OF THE INVENTION

[0011] One subject of the present invention is therefore the use of a hydrophobic polyether-block-polyamide copolymer (PEBA) for the manufacture of a fabric material (having a melting point T_m) capable of cooling after said material has been brought into contact with an aqueous medium at a temperature lying in the range from 15° C. to T_m-20° C., said medium comprising at least 85 wt % water relative to the weight of the aqueous medium, preferably at least 90 wt % water and more preferably at least 95 wt % water relative to the weight of the medium; said PEBA comprising 20 to 80 wt % polyamide blocks and 80 to 20 wt % polyether blocks, preferably 30 to 70 wt % of polyamide blocks and 70 to 30 wt % of polyether blocks, and having a saturated water absorption of less than 6 wt %, preferably less than 3 wt %, according to the ISO 62 standard relative to the weight of PEBA.

[0012] Advantageously, said fabric material is such that it cools to a temperature below the ambient temperature for at least 15 minutes, preferably for at least 30 minutes, more preferably for at least one hour and even more preferably for at least two hours, after said contacting operation, the ambient temperature being in the range from 10 to 80° C., preferably from 10 to 50° C. and even more preferably from 15 to 40° C.

[0013] Advantageously, said material is such that it has accelerated and prolonged properties of desorbing and evaporating said aqueous medium in the form of cold gas at a temperature below the ambient temperature, preferably below 20° C.

[0014] Advantageously, said material takes the form of a porous membrane, a woven fabric or a nonwoven fabric.

[0015] Advantageously, said material comprises fibers and/or filaments and/or particles based on said PEBA.

[0016] Another subject of the present invention is a method for cooling the skin of a human being, comprising the application to said skin of a cooling fabric material impregnated with an aqueous medium, either naturally (for example by sweat) or by an intentional addition (for example an addition of water, an active agent, especially a cosmetic, pharmaceutical or medical agent, a moisturizing agent, etc.), said material comprising at least 10 wt %, preferably at least 30 wt %, more preferably at least 50 wt %, more preferably still at least 80 wt % and ideally 100 wt %, of a hydrophobic polyether-block-polyamide copolymer (PEBA), said material having a melting point T_m such that T_m-20° C. is above the ambient temperature, said PEBA comprising 20 to 80 wt % of polyamide blocks and 80 to 20 wt % of polyether blocks, preferably 30 to 70 wt % of polyamide blocks and 70 to 30 wt % of polyether blocks relative to the weight of PEBA, and having a saturated water absorption of less than 6 wt %, preferably less than 3 wt %, according to the ISO 62 standard relative to the weight of PEBA, and said aqueous medium comprising at least 85 wt % water, preferably at least 90 wt % water, more preferably at least 95 wt % water, relative to the weight of said aqueous medium, the temperature of the aqueous medium being in the range from 15° C. to T_m-20° C.

[0017] Another subject of the present invention is a fabric material, especially one useful for implementing this cooling method, characterized in that it comprises a hydrophobic polyether-block-polyamide copolymer (PEBA) comprising 20 to 80 wt % polyamide blocks and 80 to 20 wt % polyether blocks, preferably 30 to 70 wt % of polyamide blocks and 70 to 30 wt % of polyether blocks, relative to the weight of PEBA; and having a saturated water absorption of less than 6%, preferably less than 3%, according to the ISO 62 standard relative to the weight of PEBA.

[0018] In particular, another subject of the present invention is a cooling fabric material comprising a fabric material as defined above, impregnated with an aqueous medium comprising at least 85 wt % water, preferably at least 90 wt % water and more preferably at least 95 wt % water, relative to the aqueous medium weight, the temperature of the aqueous medium being in the range from 15° C. to T_m-20° C., T_m being the melting point of the fabric material, the weight content of hydrophobic PEBA representing at least 10% of the total weight of the cooling fabric material.

[0019] Advantageously, said PEBA is made as a compound with at least one filler and/or at least one pigment and/or at least one additive.

[0020] Advantageously, said fabric comprises synthetic fibers obtained from bioresource raw materials.

[0021] Advantageously, said fabric further comprises natural fibers, artificial fibers manufactured from natural raw materials, mineral fibers, metal fibers and/or synthetic fibers other than hydrophobic PEBA fibers.

[0022] Advantageously, said fabric is manufactured solely from bioresource raw materials.

[0023] Advantageously, said fabric comprises at least one structure chosen from:

[0024] mixtures of monofilaments and/or multifilaments comprising hydrophobic PEBA with other fabric materials; and/or

[0025] at least one ply of predominantly hydrophobic fabric material, comprising at least 10% hydrophobic PEBA, superposed on at least one ply of predominantly hydrophilic fabric material; and/or

[0026] sandwich structures based on said plies; and

[0027] combinations of these structures.

[0028] Advantageously, said fabric constitutes a felt, web, a net, a filter, a film, a gauze, a cloth, a bandage, a wipe, a ply, a woven, a knit, an article of clothing, a garment, a pair of tights, stockings, especially support stockings, an article of bed linen, an article of furniture, a napkin, a package, a curtain, an interior lining, a functional engineering textile, a geotextile and/or an agricultural textile.

[0029] Yet another subject of the invention is the use of a fabric according to the invention in the medical, cosmetic, hygiene, baggage, confection, clothing, domestic or household equipment, furnishing, carpet, automotive or industrial fields, especially for industrial filtration and cooling, ventilation and air-conditioning systems, agricultural and/or building matter.

DETAILED DESCRIPTION OF THE INVENTION

[0030] Polyether-block-polyamide copolymers, abbreviated to PEBA, result from the polycondensation of polyamide blocks having reactive end groups with polyether blocks having reactive end groups, such as, inter alia:

[0031] 1) polyamide blocks having diamine chain ends with polyoxyalkylene blocks having dicarboxylic chain ends;

[0032] 2) polyamide blocks having dicarboxylic chain ends with polyoxyalkylene blocks having diamine chain ends, obtained by cyanoethylation and hydrogenation of aliphatic dihydroxylated α,ω-polyoxyalkylene blocks, called polyetherdiols; and 3) polyamide blocks having dicarboxylic chain ends with polyetherdiols, the products obtained being, in this particular case, polyetheresteramides.

[0033] The polyamide blocks having dicarboxylic chain ends result, for example, from the condensation of polyamide precursors in the presence of a chain-stopping dicarboxylic acid. The polyamide blocks having diamine chain ends result, for example, from the condensation of polyamide precursors in the presence of a chain-stopping diamine.

[0034] The number-average molecular weight M_n of the polyamide blocks is between 400 and 20 000 g/mol and preferably between 500 and 10 000 g/mol.

[0035] The polyamide-block-polyether polymers may also comprise randomly distributed units.

[0036] Advantageously, three types of polyamide block may be used.

[0037] According to a first type, the polyamide blocks resulting from the condensation of a dicarboxylic acid, in particular those having 4 to 20 carbon atoms, preferably those having 6 to 18 carbon atoms, and of an aliphatic or aromatic diamine, in particular those having 2 to 20 carbon atoms, preferably those having 6 to 14 carbon atoms.

[0038] As examples of dicarboxylic acids, mention may be made of 1,4-cyclohexyldicarboxylic acid, butanedioic, adipic, azelaic, suberic, sebacic, dodecanedicarboxylic and octadecanedicarboxylic acids, and terephthalic and isophthalic acids, but also dimerized fatty acids.

[0039] As examples of diamines, mention may be made of tetra-methylenediamine, hexamethylenediamine, 1,10-decamethylenediamine, dodecamethylenediamine, trimethylhexamethylenediamine, isomers of bis(4-aminocyclohexyl) methane (BACM), bis(3-methyl-4-aminocyclohexyl) methane (BMACM) and 2,2-bis(3-methyl-4-aminocyclohexyl)propane (BMACP) and para-aminodicyclohexylmethane (PACM) and isophoronediamine (IPDA), 2,6-bis(aminomethyl)norbornane (BAMN) and piperazine (Pip).

[0040] Advantageously, the blocks are advantageously: PA-4,12; PA-4,14; PA-4,18; PA-6,10; PA-6,12; PA-6,14; PA-6,18; PA-9,12; PA-10,10; PA-10,12; PA-10,14; and PA-10,18 blocks.

[0041] According to a second type, the polyamide blocks result from the condensation of one or more α,ω-aminocarboxylic acids and/or one or more lactams having 6 to 12 carbon atoms in the presence of a dicarboxylic acid having 4 to 12 carbon atoms or in the presence of a diamine. As examples of lactams, mention may be made of caprolactam, enantholactam and lauryllactam. As examples of α,ω-aminocarboxylic acids, mention may be made of aminocaproic, 7-aminoheptanoic, 11-aminoundecanoic and 12-aminododecanoic acids.

[0042] Advantageously, the polyamide blocks of the second type are blocks of nylon-11, nylon-12 or nylon-6.

[0043] According to a third type, the polyamide blocks result from the condensation of at least one α,ω-aminocarboxylic acid (or a lactam), at least one diamine and at least one dicarboxylic acid.

[0044] In this case, the polyamide (PA) blocks are prepared by polycondensation:

[0045] of one or more aromatic or linear aliphatic diamines having X carbon atoms;

[0046] of one or more dicarboxylic acids having Y carbon atoms; and

[0047] of one or more comonomers {Z} chosen from lactams and α,ω-aminocarboxylic acids having Z carbon atoms and equimolar mixtures of at least one diamine having X1 carbon atoms and of at least one dicarboxylic acid having Y1 carbon atoms, X1 and Y1 being different from X, Y respectively;

[0048] said at least one comonomers {Z} being introduced in a weight proportion ranging up to 50%, preferably up to 20% and even more advantageously up to 10% relative to all of the polyamide precursor monomers;

[0049] in the presence of a chain stopper chosen from dicarboxylic acids.

[0050] Advantageously, a dicarboxylic acid having Y carbon atoms is used as chain stopper, which is introduced in excess relative to the stoichiometry of the diamine or diamines.

[0051] According to a variant of this third type, the polyamide blocks result from the condensation of at least two α,ω-aminocarboxylic acids or of at least two lactams having 6 to 12 carbon atoms or of a lactam and an aminocarboxylic acid not having the same number of carbon atoms possibly in the presence of a chain stopper. As examples of aliphatic α,ω-aminocarboxylic acids, mention may be made of aminocaproic, 7-aminoheptanoic, 11-aminoundecanoic and 12-aminododecanoic acids. As examples of lactams, mention may be made of caprolactam, enantholactam and lauryllactam. As examples of aliphatic diamines, mention may be made of hexamethylenediamine, dodecamethylenediamine and trimethylhexamethylenediamine. As an example of a cycloaliphatic diacid mention may be made of 1,4-cyclohexyldicarboxylic acid. As examples of aliphatic diacids, mention may be made of butanedioic, adipic, azelaic, suberic, sebacic and dodecanedicarboxylic acids, and dimerized fatty acids (these dimerized fatty acids preferably have a dimer content of at least 98% and are preferably hydrogenated—they are sold under the trademark PRIPOL by Unichema or under the trademark EMPOL by Henkel) and α,ω-polyoxyalkylene diacids. As examples of aromatic diacids, mention may be made of terephthalic (T) and isophthalic (I) acids. As examples of cycloaliphatic diamines, mention may be made of isomers of bis(4-aminocyclohexyl)methane (BACM), bis(3-methyl-4-aminocyclohexyl)methane (BMACM), 2,2-bis(3-methyl-4-aminocyclohexyl)propane (BMACP), and para-aminodicyclohexylmethane (PACM). Other commonly used diamines may be isophoronediamine (IPDA), 2,6-bis(aminomethyl)norbornane (BAMN) and piperazine.

[0052] As examples of polyamide blocks of the third type, mention may be made of the following:

[0053] 6,6/6 in which 6,6 denotes hexamethylenediamine units condensed with adipic acid and 6 denotes units resulting from the condensation of caprolactam; and

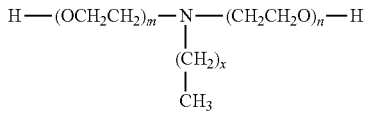
[0054] 6,6/6,10/11/12 in which 6,6 denotes hexamethylenediamine condensed with adipic acid, 6,10 denotes hexamethylenediamine condensed with sebacic acid, 11 denotes units resulting from the condensation of aminoundecanoic acid and 12 denotes units resulting from the condensation of lauryllactam.

[0055] The polyether blocks may represent 5 to 85 wt % of the polyamide-block-polyether copolymer. The molecular weight M_n of the polyether blocks is between 100 and 6000 g/mol and preferably between 200 and 3000 g/mol.

[0056] The polyether blocks consist of alkylene oxide units. These units may for example be ethylene oxide units, propylene oxide units or tetrahydrofuran units (resulting in polytetramethylene glycol chains). Thus the following may be used: PEG (polyethylene glycol) blocks, that is to say those consisting of ethylene oxide units; PPG (propylene glycol) blocks, that is to say those consisting of propylene oxide units; PO3G (polytrimethylene glycol) blocks, that is to say those consisting of polytrimethylene ether glycol units (such copolymers with polytrimethylene ether blocks are described in the document U.S. Pat. No. 6,590,065); and PTMG blocks, that is to say those consisting of tetramethylene glycol units, also called polytetrahydrofuran. The PEBA copolymers may comprise in their chain several types of polyether, it being possible for the copolyethers to be blocky or random.

[0057] It is also possible to use blocks obtained by the oxyethylation of bisphenols, such as for example bisphenol A. The latter products are described in the patent EP 613 919.

[0058] The polyether blocks may also consist of ethoxylated primary amines. As examples of ethoxylated primary amines, products of the following formula may be mentioned:



in which m and n are between 1 and 20 and x is between 8 and 18. These products are commercially available under the trademark NORAMOX® from CECA and under the brand name GENAMIN® from Clariant.

[0059] The polyether soft blocks may comprise polyoxyalkylene blocks having NH_2 chain ends, such blocks being able to be obtained by cyanoacetylation of aliphatic dihydroxylated α,ω-polyoxyalkylene blocks, called polyetherdiols. More particularly, Jeffamines may be used (for example Jeffamine® D400, D2000, ED 2003 and XTJ 542, commercial products from Huntsman, also described in the patent documents JP 2004346274, JP 2004352794 and EP 1 482 011).

[0060] The polyetherdiol blocks are either used as such and copolycondensed with polyamide blocks having carboxylic end groups, or they are aminated so as to be converted into polyetherdiamines and condensed with polyamide blocks having carboxylic end groups. The general two-step method of preparing PEBA copolymers having ester links between the PA blocks and the PE blocks is known and described, for example, in French patent FR 2 846 332. The general method of preparing the PEBA copolymers of the invention having amide links between the PA blocks and the PE blocks is known and described, for example, in European patent EP 1 482 011. The polyether blocks may also be mixed with polyamide precursors and a diacid chain stopper to make polymers with polyamide blocks and polyether blocks having randomly distributed units (one-step process).

[0061] Of course, the name PEBA in the present description of the invention also relates to PEBAX® polymers sold by Arkema, to Vestamid® polymers sold by Evonik®, to

Grilamid® polymers sold by EMS, to Kellaflex® polymers sold by DSM or to any other PEBA from other suppliers.

[0062] The expression "hydrophobic PEBA" in the context of the invention is understood to mean a PEBA which has at the same time a saturated water absorption of less than 6 wt %, preferably less than 3 wt %, according to the ISO 62 standard, relative to the weight of PEBA and comprises 20 to 80 wt % of polyamide blocks and 80 to 20 wt % of polyether blocks, preferably 30 to 70 wt % of polyamide blocks and 70 to 30 wt % of polyether blocks.

[0063] Advantageously, the PEBA copolymers have PA-6, PA-11, PA-12, PA-6,12, PA-6,6/6, PA-10,10 and/or PA-6,14 polyamide (PA) blocks, preferably PA-II and/or PA-12 polyamide blocks, and PTMG, PPG and/or PO3G polyether (PE) blocks. The PEBAs based on PE blocks consisting predominantly of PEG are in the range of hydrophilic PEBAs. Fabric materials based on hydrophilic PEBAs, i.e. based on PEBAs that do not meet the criteria of hydrophobic PEBAs defined above, are not capable of cooling under the conditions of use or using the method of the present invention, as table 1 below shows, and may even on the contrary become swollen upon contact with water.

BRIEF DESCRIPTION OF THE DRAWING

[0064] FIG. **1** is a photograph of a web of 80 g/m^2 weight at three increasing magnifications (1, 2 and 3). The last magnification shows how, on the surface of the hydrophobic PEBA (PA-12/PTMG) fibers, water is dispersed as microdroplets with a size of less than 20 μm, or even less than 10 μm, thereby resulting in their extremely rapid evaporation thanks to their low surface tension. This evaporation is caused by direct heat transfer between these droplets and the ambient air, the hydrophobic PEBA used according to the invention being a poor heat conductor. It is in particular the heat transfer from the skin to these droplets, on the surface of a fabric according to the invention, which gives a surprising "dry cold" sensation.

[0065] Advantageously, the hydrophobic PEBA is made as a compound with at least one filler and/or at least one pigment and/or at least one additive. The polymeric matrix of the PEBA may especially comprise additives. Said additives may, for example, be reinforcing fillers, fire retardants, UV protection agents, UV stabilizers, heat stabilizers, pigments, lubricants, antioxidants, fluidity-improving agents, casting agents, film-forming agents, filmifying auxiliaries, gums, semicrystalline polymers, preservatives and mixtures thereof. Of course, any other type of additive used in the field of fabrics can also be envisioned.

[0066] The present invention also in particular relates to the use of said hydrophobic PEBA for manufacturing fabric materials, such as yarns, fibers, filaments (monofilaments or multifilaments), films, membranes, porous membranes, woven and nonwoven fabrics. The present invention also relates to the manufacture and to the use of hydrophobic PEBA particles that have been melted so that they adhere to the surface of fabric materials lastingly (wash-resistant fabrics).

[0067] Advantageously, the weight content of hydrophobic PEBA represents at least 10%, preferably at least 30%, more preferably at least 50%, even more preferably at least 80% and ideally 100% of the total weight of the fabric according to the invention.

[0068] In the present description, the term T_m represents the melting point of the fabric material. This may for example be in the range from 100 to 170° C.

[0069] Said PEBA or the thermoplastic matrix compositions based on said PEBA may be formed into fabric material directly after polymerization, with no intermediate solidification and remelting steps. It may also take the form of granules, intended to be remelted for a subsequent final forming operation, for example for manufacturing molded fabric articles or for manufacturing yarns, fibers and/or filaments.

[0070] All melt spinning processes may be used, in particular by making the composition of the invention pass through spinnerets having one or more orifices. To manufacture multifilament yams, spinning or spin-draw or spin-draw-texturing processes, whether integrated or not and irrespective of the spinning rate, may be mentioned. The yams may be produced by high-speed spinning, with spinning rates equal to or greater than 3000 m/min, preferably equal to or greater than 4000 m/min. Such processes are often denoted by the following terms: POY (partially oriented yam), FOY (fully oriented yam), ISD (integrated spin-draw) and HOY (highly oriented yarn with a spinning rate of greater than 5500 m/min). These yarns may also be textured, depending on the usage for which they are intended. The yarns obtained by these processes are most particularly suitable for producing fabric surfaces, whether woven or knitted. According to the invention, the PEBA thermoplastic polymeric matrix may be used for manufacturing monofilamentary or monofilament yarns, multifilamentary or multifilament yarns, continuous fibers (on reels) and/or discontinuous (chopped) fibers. Chopped PEBA fibers are particularly well suited for being mixed with natural fibers. One process particularly well suited to the manufacture of PEBA monofilaments and multifilaments is that described in patent application US 2010/0119804.

[0071] For individual fibers or monofilaments, the linear densities may range from 1.5 dtex to 100 dtex per filament, the high linear densities being particularly well suited for industrial application. Multifilamentary yarns preferably have a linear density of 6 dtex per filament or less, more preferably 1.5 dtex per filament or less. To manufacture fibers, the filaments may for example be combined in the form of a roving or lap, directly after spinning, or subsequently drawn, textured or crimped and chopped. The fibers obtained may be used to manufacture nonwovens or staple fiber yarns. The compositions may also be used to manufacture flock. The yarns, fibers and/or filaments of the invention may undergo various treatments, such as for example drawing in a continuous step, or subsequently, size deposition, oiling, gelating, texturing, crimping, drawing, fixing or relaxing heat treatment, throwing, twisting and/or dyeing. In the case of dyeing, vat dyeing or jet dyeing processes may in particular be mentioned. The preferred dies are acid dies, metalliferous dies, nonmetalliferous dies.

[0072] The present invention also relates to fabric articles made of a PEBA matrix or a thermoplastic composition comprising the PEBA according to the invention that are obtained by a forming operation using a process chosen from the group comprising the following: extrusion processes, such as for the extrusion of sheets and films; molding processes, such as for compression molding; and injection processes, such as for injection molding. Films may thus be obtained by the aforementioned processes using a sheet die. The films obtained my undergo various treatment steps, such as a uniaxial or biaxial

drawing treatment, a stabilizing heat treatment, an antistatic treatment or a sizing treatment.

[0073] The fabrics comprising hydrophobic PEBA according to the invention provide a cold or cooling effect under certain conditions: the cooling effect is caused after the hydrophobic-PEBA-based fabric material has been brought into contact (either by simple contacting or by impregnation, spraying or even dipping) with an aqueous medium, irrespective of the way in which the aqueous medium has been added to the fabric material.

[0074] The term "aqueous medium" is understood in the context of the invention to mean a liquid or a gas, vapor, or even a solid, said medium comprising at least 85 wt % water, preferably at least 90 wt % water and more preferably at least 95 wt % water relative to the weight of the medium, and the temperature of the aqueous medium preferably lies in the 1° C. to T_m-20° C. range, preferably the 15° C. to T_m-20° C. range, T_m being the melting point of a fabric material according to the invention.

[0075] The aqueous medium may naturally impregnate the fabric or may come naturally into contact with the fabric material. This is the case for example of sweat on a garment. The aqueous medium may also be intentionally added to the fabric by any means, such as impregnation, dipping or spraying, with the aqueous medium in gas, vapor or liquid form, or else by any other method of adding liquid, gas or vapor to a fabric material. This is the case of a medical, pharmaceutical or cosmetic active agent or of a perfume that may for example be added to a bandage or a cooling wipe respectively.

[0076] The term "ambient temperature" is understood in the context of the invention to mean the temperature of the air or the medium surrounding the fabric, whether this temperature is controlled (air-conditioning, cold chamber), programmed (operating temperature of a process or device) or not controlled (due to the external geographical and weather conditions). More precisely, the ambient temperature is understood to mean a temperature lying within the −60° C. to 150° C. range, preferably the −40° C. to 140° C. range. The fabric materials according to the invention comprising at least 50% hydrophobic PEBA are capable of withstanding these temperatures, the PEBAs retaining all their properties (especially flexibility and their dimensions) at these temperatures.

[0077] Preferably, the fabric material according to the invention is such that it cools to a temperature below the ambient temperature for at least 15 minutes, preferably for at least 30 minutes, more preferably for at least one hour and even more preferably for at least two hours, after said contacting, the ambient temperature being within the 10 to 80° C., preferably 10 to 50° C. and more preferably 15 to 40° C. range.

[0078] Advantageously, said material is such that it has accelerated and prolonged properties of desorbing and evaporating said aqueous medium in cold gas form from a temperature below the ambient temperature, preferably below 20° C.

[0079] The present invention also relates to a fabric or a fabric article obtained at least partly from hydrophobic PEBA, in the form of yarns, fibers and/or filaments as defined above. These articles may be fabrics or fabric surfaces, such as woven, knitted, nonwoven or matt surfaces.

[0080] Said fabric is advantageously used in the medical, cosmetic, pharmaceutical hygiene, baggage, confection, clothing, domestic or household equipment, furnishing, carpet, automotive or industrial fields, especially for industrial filtration, agricultural and/or building matter.

[0081] These articles may for example be carpets, furniture coverings, surface coverings, sofas, curtains, mattresses and pillows, drinks coolers, pipe cooling sleeves, and medical fabric materials. The fabric according to the invention advantageously constitutes a felt, a filter, a film, a gauze, a cloth, a web, a net, a bandage, especially a bandage for soothing pain or burns, a ply, a woven, a knit, an article of clothing, a garment, a pair of tights, stockings, especially support stockings, an article of bed linen, an article of furniture, a napkin, a package, a curtain, an interior lining, a functional engineering textile, a geotextile and/or an agricultural textile.

[0082] The cold effect is particularly surprising on a web, a net, knitted fabric using monofilaments or multifilaments or on a perforated film. For example, after these structures have been immersed in hot water at around 40° C. and then briefly dried, they produce a cold effect in a few seconds, the surface temperature of the fabric being lowered to 16° C. in less than around ten seconds. Immersion in water at the ambient temperature (for example 20° C.) gives the same results. Hot water, especially at a temperature above 30° C., provides an additional surprise effect.

[0083] Advantageously, said fabric comprising PEBA-based fibers, filaments and/or films has a high specific surface area. It has been demonstrated that this further increases the rate of evaporation of an aqueous liquid at the surface of the textile fabric comprising these fibers and/or filaments according to the invention. Likewise, the surface of the fibers or filaments may have a particular structure such as grooves, especially straight, ellipsoidal, etc. grooves, to increase the rate of evaporation and therefore the cold effect of the fabric materials according to the invention.

[0084] These fabrics according to the invention manufactured from hydrophobic PEBA, preferably predominantly so, (comprising at least 50 wt % PEBA) also have other advantageous properties. They are light, flexible and soft to the touch; they are resistant to tearing, cutting, abrasion and pilling

[0085] Advantageously, said fabric further includes: natural fibers, such as cotton, wool and/or silk fibers; artificial fibers manufactured from natural raw materials; mineral fibers, such as carbon, glass, silica and/or magnesium fibers; metal fibers; and/or synthetic fibers other than PEBA fibers. The synthetic fibers may especially comprise polyester, polyether, polyetherester, polyamide or acrylic fibers, or fibers of any other synthetic material generally used in the fabric sector.

[0086] The fabrics according to the invention may especially comprise combinations of hydrophobic PEBA with hydrophilic synthetic fibers (for example hydrophilic PEBA fibers). The latter act as a moisture transfer agent. The hydrophilic synthetic fibers absorb the moisture and, on contact with the PEBA, the latter causes evaporation cooling the fabric. As an example of a structure that can be used in a garment, the hydrophilic fibers are predominantly in contact with the skin (for example the inside of a T-shirt) in order to absorb the moisture and transfer it to the hydrophobic PEBA fibers that are predominantly on the outside of the garment, on the ambient medium side. The fabrics according to the invention may have sandwich structures comprising a ply of predominantly hydrophilic fibers sandwiched between two plies of predominantly hydrophobic fibers, comprising at least 10% hydrophobic PEBA, or, conversely, comprising a ply of predominantly hydrophobic fibers, comprising at least 10%

hydrophobic PEBA, sandwiched between two plies of predominantly hydrophilic fibers.

[0087] Here the term "predominantly" means that the ply contains more than 50 wt % of hydrophobic or hydrophilic fibers, depending on the case. Unlike a purely hydrophilic fabric which accumulates water and causes a cold effect only because of the presence of the water, thereby causing a "moist" cold sensation, the hydrophobic-PEBA-based fabrics of the invention cause a surprising dry cold effect. The hydrophobic PEBA evaporates the water more rapidly, causing an intense cold sensation on the surface of the fabric and making the wetted effect of the fabric disappear almost instantaneously.

[0088] Advantageously, said fabric comprises synthetic fibers obtained from bioresource raw materials. Preferably, the fabric according to the invention is manufactured solely from bioresource raw materials.

[0089] The expression "renewable raw materials" or the expression "bioresource raw materials" is understood to mean materials that comprise bioresource carbon or renewable carbon. Unlike materials obtained from fossil materials, materials composed of renewable raw materials contain ^{14}C. The "renewable carbon content" or "bioresource carbon content" is determined by applying the ASTM D 6866 (ASTM D 6866-06) and ASTM D 7026 (ASTM D 7026-04) standards. The first standard describes a test for measuring the $^{14}C/^{12}C$ ratio of a specimen and compares it with the $^{14}C/^{12}C$ ratio of a reference specimen of 100% bioresource origin in order to give a relative percentage of bioresource carbon in the specimen. The standard is based on the same concepts as in carbon 14 dating, but without applying the dating equations. The ratio thus calculated is called the "pMC" (percent Modern Carbon). If the material to be analyzed is a mixture of biomaterial and fossil material (with no radioactive isotope), then the pMC value obtained is directly correlated with the amount of biomaterial present in the specimen. The ASTM D 6866 standard provides several techniques for measuring the content of the ^{14}C isotope, these being based either on LSC (liquid scintillation counting), i.e. liquid scintillation spectrometry, or on AMS/IRMS (accelerator mass spectrometry coupled with isotope ratio mass spectrometry). The measuring method preferentially used in the case of the present invention is mass spectrometry, described in the ASTM D 6866-06 standard (i.e. accelerator mass spectroscopy).

[0090] To give an example, the fabrics of the invention containing PEBA based on PA-11 are at least partly obtained from bioresource raw materials and have a bioresource carbon content of at least 1%, corresponding to a $^{12}C/^{14}C$ isotope ratio of 1.2×10^{-14}. Preferably, in the fabrics according to the invention at least 50% of the total carbon mass is bioresource carbon mass, corresponding to a $^{12}C/^{14}C$ isotope ratio of at least 0.6×10^{-12}. This content is advantageously higher, especially up to 100%, corresponding to a $^{12}C/^{14}C$ isotope ratio of 1.2×10^{-12} in the case of PEBAs having PA-11 blocks and PE blocks comprising PO3G, PTMG and/or PPG obtained from renewable raw materials. The fabrics according to the invention may therefore be made of 100% bioresource carbon or on the contrary result from a mixture with carbon of fossil origin.

EXAMPLES

[0091] The examples below illustrate the present invention without limiting the scope thereof. Unless otherwise indicated, all the percentages are by weight.

Measuring the Temperature of Various Fabrics

[0092] The fabrics manufactured from PEBA according to the invention are compared with fabrics based on other materials normally used in fabrics, namely PES (polyester), PA (polyamide) and cotton.

[0093] In examples Ex1, Ex2, Ex3, Ex4 and Ex5 according to the invention and in comparative example Cp2, the PEBA is PA12-PTMG, i.e. it comprises PA-12 blocks and PTMG blocks. In examples Ex1.1, Ex2.1 and Ex3.1, the PEBA is PA-11/PTMG. In comparative examples 3, 4 and 5, the PEBA is PA-6/PTMG, PA-12/PEG and PA-6/PEG respectively. Comparative example Cp1 is polyester, Cp6 is PA-11, Cp1 is cotton and Cp8 is a PA-6/6,6/12 copolyamide of Platamid® H005 trademark.

[0094] The contents (in wt percent) of the PA and PE blocks are indicated in table 1.

[0095] The temperature measurements were carried out on the fabric using an infrared gun (Cole-Parmer®).

[0096] The aqueous medium used in the examples was liquid water.

[0097] The fabric material was in the form of a light web weighing 80 g/m^2 for all the tests except in the case of example 2.

[0098] Example 2 was a nonwoven consisting of tighter fibers than those of the web and with a greater weight, making contact with the aqueous medium more difficult, and with a smaller contact area. The fabric was less impregnated with the aqueous medium.

[0099] Protocol: with a 23° C. ambient temperature:

- **[0100]** at T0: the fabric material was immersed in water (material/aqueous medium contact) for 5 seconds;
- **[0101]** drying for 5 seconds; and then
- **[0102]** measurement of the surface temperature of the fabric using the infrared gun, after 30 seconds, 30 minutes, 1 hour, 1 hour 30 minutes and then 2 hours, respectively.

[0103] The results are expressed in table 1 below.

TABLE 1

Characterization and measurement of the cold effect of the fabric

	Fabric material				Liquid (water)	Temperature of the fabric material as a function of the time elapsed from T0 (material-liquid contact time)				
	PA (wt %)	PE (wt %)	Saturated water absorption (%) (ISO 62)	Temperature before contact with the liquid	Temperature of the liquid	T0 + 30 s	T0 + 30 min	T0 + 1 h	T0 + 1 h 30	T0 + 2 h
Cp1	polyester			23° C.	30° C.	24° C.		23° C.		23° C.
Ex 1	23	77	1.2	23° C.	30° C.	16° C.	16° C.	17° C.	17° C.	19° C.

TABLE 1-continued

Characterization and measurement of the cold effect of the fabric

	Fabric material				Liquid (water)	Temperature of the fabric material as a function of the time elapsed from T0 (material-liquid contact time)				
	PA (wt %)	PE (wt %)	Saturated water absorption (%) (ISO 62)	Temperature before contact with the liquid	Temperature of the liquid	T0 + 30 s	T0 + 30 min	T0 + 1 h	T0 + 1 h 30	T0 + 2 h
Ex 1.1	23	77	1.2	23° C.	15° C.	15° C.	16° C.	17° C.	18° C.	19° C.
Ex 2	30	70	1.2	23° C.	30° C.	16° C.	16° C.	20° C.	22° C.	22° C.
Ex 2.1	37.5	62.5	1.3	23° C.	30° C.	16° C.	16° C.	17° C.	18° C.	19° C.
Ex 3	50	50	1.2	23° C.	30° C.	16° C.	16° C.	17° C.	18° C.	19° C.
Ex 3.1	50	50	1.4	23° C.	30° C.	16° C.	16° C.	17° C.	18° C.	19° C.
Ex 4	70	30	1.2	23° C.	30° C.	16° C.	16° C.	17° C.	18° C.	20° C.
Ex 5	80	20	1.1	23° C.	30° C.	18° C.	18° C.	18° C.	19° C.	21° C.
Cp2	98.5	11.5	1.1			22° C.		23° C.		23° C.
Cp3	67	33	6.7	swollen						
Cp4	50	50	48	swollen						
Cp5	50	50	120	swollen						
Cp6	100	0	1			22° C.		23° C.		23° C.

[0104] OBSERVATIONS: Apart from the fabrics according to the invention, the other fabrics provided no cold effect.

[0105] The fabrics of comparative examples Cp1 to Cp6 were swollen, were distorted and had a soaked and heavy appearance; after contact with the liquid, the observed temperature drop of the fabric was zero (in Cp1) or very small (Cp2 to Cp6).

[0106] Conversely, the hydrophobic-PEBA-based fabrics of the examples according to the invention, "Ex", cooled and had a cooling effect lasting for at least 2 hours, had a dry, pleasant and soft feel, while remaining very light. Their temperature dropped by 5 to 7° C. over at least 1 h 30 relative to the initial temperature of 23° C., corresponding to the ambient temperature, even after impregnation with water at a temperature of 30° C.

[0107] On gently shaking a hydrophobic-PEBA-based fabric according to the invention, for example at T0+1 h 30, it was found that its temperature dropped again to 16° C. owing to the additional evaporation produced.

[0108] In table 2 below, the amount of water that had evaporated over the course of time, for various fabrics (webs) made of cotton (Cp7), PA-6/6,6/12 copolyamide (Cp8) and hydrophobic PEBA (Ex1), after they had been wetted and dried according to the same protocol, was measured (by weighing the fabric). These weight measurements were carried out on fabrics that remained "static", that is to say stationary after drying.

TABLE 2

Measurement and comparison of water evaporation on the fabric

		Weight (g) of the fabric		Weight as a function of the elapsed time from T0			
Type of fabric		Before wetting	After wetting (T0)	T0 + 60 min	T0 + 120 min	T0 + 150 min	T0 + 180 min
Cotton	Total weight of the fabric (g)	18.55	27.84	26.94	26.14	25.53	24.8
Cp7	Weight of water (g) on the fabric	0	9.29	8.39	7.59	6.99	6.25
	Weight of evaporated water (g)	0	0	0.9	1.7	2.31	3.04
	Percentage of evaporated water (%)	0	0	9.7	18.3	24.9	32.7
CoPA	Fabric weight (g)	18.1	26.1	25.12	24.1	23.44	22.63
Cp8	Weight of water (g) on the fabric	0	8	7.02	6	5.34	4.53
	Weight of evaporated water (g)	0	0	0.98	2	2.66	3.47
	Percentage of evaporated water (%)	0	0	12.25	25	33.25	43.38
Pebax	Fabric weight (g)	17.7	24.48	23.47	22.3	21.5	20.77
Ex1	Weight of water (g) on the fabric	0	6.78	5.77	4.6	3.8	3.07
	Weight of evaporated water (g)	0	0	1.01	2.18	2.98	3.71
	Percentage of evaporated water (%)	0	0	14.9	32.2	44	54.7

[0109] OBSERVATIONS: The PEBA fabric (Ex1) according to the invention had accelerated water evaporation properties, the water taking the form of cold gas at a temperature below 20° C., whereas the evaporation of water from a polyamide fabric or a cotton fabric was much slower.

[0110] The PEBA used in the composition of a fabric according to the invention had a surprising dry cold effect lasting for several hours and capable of being intensified and extended through the effect of movement (for example if it was shaken gently at T0+1 hours) or else through the effect of a further contact with an aqueous medium, such as liquid water, or the sweat of a sportsman for example.

[0111] Advantageously, the cooling effect of the fabric according to the invention is intensified and extended by shaking the fabric that has previously been brought into contact with an aqueous medium.

[0112] The behavior of the fabrics according to the invention is therefore the ideal behavior desirable for engineering fabrics, especially in the sports field, in particular for sports clothing.

1. A fabric material made from a hydrophobic polyether-block-polyamide copolymer (PEBA), said fabric material capable of cooling after said material has been brought into contact with an aqueous medium at a temperature lying in the range from 15° C. to T_m-20° C., T_m being the melting point of the fabric material, said aqueous medium comprising at least 85 wt % water relative to the weight of the aqueous medium, said PEBA comprising 20 to 80 wt % polyamide blocks and 80 to 20 wt % polyether blocks and having a saturated water absorption of less than 6 wt % according to the ISO 62 standard relative to the weight of PEBA.

2. The fabric material as claimed in claim **1**, in which said fabric material is such that it cools to a temperature below the ambient temperature for at least 15 minutes, preferably for at least 30 minutes, more preferably for at least one hour and even more preferably for at least two hours, after said contacting operation, the ambient temperature being in the range from 10 to 80° C.

3. The fabric material as claimed in claim **1**, in which said material is such that it has accelerated and prolonged properties of desorbing and evaporating said aqueous medium in the form of cold gas at a temperature below the ambient temperature, preferably below 20° C.

4. The fabric material as claimed in claim **1**, in which said material takes the form of a porous membrane, a woven fabric or a nonwoven fabric.

5. The fabric material as claimed in claim **1**, in which said material comprises fibers and/or filaments and/or particles based on said PEBA.

6. A method for cooling the skin of a human being, comprising the application to said skin of a cooling fabric material impregnated with an aqueous medium, said material comprising at least 10 wt % of a hydrophobic polyether-block-polyamide copolymer (PEBA), said material having a melting point T_m such that T_m-20° C. is above the ambient temperature, said PEBA comprising 20 to 80 wt % of polyamide blocks and 80 to 20 wt % of polyether blocks, and having a saturated water absorption of less than 6 wt % according to the ISO 62 standard relative to the weight of PEBA, and said aqueous medium comprising at least 85 wt % water, relative to the weight of said aqueous medium, the temperature of the aqueous medium being in the range from 15° C. to T_m-20° C.

7. A fabric material characterized in that it comprises a hydrophobic polyether-block-polyamide copolymer (PEBA) comprising 20 to 80 wt % polyamide blocks and 80 to 20 wt % polyether blocks, and having a saturated water absorption of less than 6% according to the ISO 62 standard relative to the weight of PEBA.

8. A cooling fabric material comprising a fabric material as claimed in claim **7**, impregnated with an aqueous medium comprising at least 85 wt % water relative to the weight of said medium, the temperature of the aqueous medium being in the range from 15° C. to T_m-20° C., T_m being the melting point of the fabric material, the weight content of hydrophobic PEBA representing at least 10% of the total weight of the cooling fabric material.

9. The fabric as claimed in claim **7**, in which said PEBA is made as a compound with at least one filler and/or at least one pigment and/or at least one additive.

10. The fabric as claimed in claim **7**, characterized in that it comprises synthetic fibers obtained from bioresource raw materials.

11. The fabric as claimed in claim **7**, characterized in that it further comprises natural fibers, artificial fibers manufactured from natural raw materials, mineral fibers, metal fibers and/or synthetic fibers other than hydrophobic PEBA fibers.

12. The fabric as claimed in claim **7**, characterized in that it is manufactured solely from bioresource raw materials.

13. The fabric as claimed in claim **7**, characterized in that it comprises at least one structure chosen from:

- mixtures of monofilaments and/or multifilaments comprising hydrophobic PEBA with other fabric materials; and/or
- at least one ply of predominantly hydrophobic fabric material, comprising at least 10% hydrophobic PEBA, superposed on at least one ply of predominantly hydrophilic fabric material; and/or
- sandwich structures based on said plies; and
- combinations of these structures.

14. The fabric as claimed in claim **7**, characterized in that it constitutes a felt, web, a net, a filter, a film, a gauze, a cloth, a bandage, a wipe, a ply, a woven, a knit, an article of clothing, a garment, a pair of tights, support stockings, an article of bed linen, an article of furniture, a napkin, a package, a curtain, an interior lining, a functional engineering textile, a geotextile and/or an agricultural textile.

15. (canceled)

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