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(54) CUT AND ABRASION RESISTANT FIBROUS STRUCTURE

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(57) **ABSTRACT**

The invention relates to a fibrous structure comprising at least one non composite p-aramid strand and at least one nylon strand maintained in a parallel relationship to each other, the non composite para-aramid strand being present in the material in an amount ranging from about 20% to 99.9% by weight, relative to the weight of the structure. The invention also relates to a process to manufacture such structure and to high cut and abrasion resistant protective clothing made of this structure like gloves, aprons and sleeves.

CUT AND ABRASION RESISTANT FIBROUS STRUCTURE

BACKGROUND OF THE INVENTION

[0001] 1. Field of the Invention

[0002] The present invention relates to a high abrasion resistant fibrous structure comprising a specific construction of a non composite p-aramid strand and a nylon strand. This structure can be used to manufacture protective clothing having a high cut resistance and a high abrasion resistance.

[0003] 2. Description of the Related Art

[0004] Aramids and more specifically para-aramids are a relatively new class of materials, which finds application in the domain of mechanical and thermal protection. High cut protection performance can be obtained from textile assemblies made of the para-aramid fibers. Therefore, para-aramid fibers are often used in the manufacture of protective clothing for industrial workers, firemen, sportsmen, military and police officers.

[0005] One drawback of para-aramid fibers is that they tend to suffer from a relatively low abrasion resistance due to their fibrillation tendency. The risk associated with this modest abrasion resistance is the reduction of the cut performance of the protective clothing with time under service. In this area of protection against wear and friction and therefore low abrasion, nylons are superior but they do not offer a sufficient cut performance.

[0006] There is still a need to provide a material having both a high and durable cut performance and a very high abrasion resistance.

[0007] There are many factors that influence the abrasion resistance of a fabric. The abrasion performance may be tailored by the selection of the type of fiber components, the fiber properties, the textile structures, the fabric mass per unit area, the number of fibers per unit volume or the relaxation allowance of the fiber components within the fiber bundle. Often, the addition of abrasion resistance materials in a given structure containing cut resistance components generally provides higher abrasion performance at the expense of the cut resistance.

[0008] U.S. Pat. No. 5,319,950 discloses a reinforcing component which is a composite yarn made of a nylon twisted yarn helically wrapped by another nylon twisted yarn, this reinforcing component being knitted in a plaited relationship with a body yarn. The manufacture of such a yarn is complex and necessitates several steps. Moreover, the reinforced fabric thus obtained is still not satisfactory as regards cut resistance.

[0009] Now, it has been found that by combining specific fiber ingredients in a specific construction style, it was possible to realize rapidly, directly and easily very high cut resistant and high abrasion resistant fibrous material. In particular, it is possible to reach the same cut resistance level with a higher level of abrasion resistance than if the same fiber ingredients are either taken separately or combined in a different construction style.

SUMMARY OF THE INVENTION

[0010] One aspect of the invention is a fibrous structure comprising at least one non composite para-aramid strand and at least one nylon strand maintained in a parallel relationship to each other, the non composite para-aramid strand being present in the structure in an amount ranging from about 20% to about 99.9% by weight, relative to the weight of the structure.

[0011] Another aspect of the invention is a process to manufacture the structure above comprising the step of processing a non composite para-aramid strand and a nylon strand in a parallel relationship to each other.

[0012] Another aspect of the invention is a process for providing a fibrous structure having high cut and abrasion resistance, comprising:

[0013] a) providing strands of at least one non composite para-aramid strand and at least one nylon strand,

[0014] b) feeding the strands into a knitting or weaving machine without prior assembly, and

[0015] c) knitting or weaving a fibrous structure without changing the order in which the strands are fed into the machine, the strands being maintained in a parallel relationship to each other during the whole knitting or weaving process.

[0016] A further aspect of the invention is a high cut and abrasion resistant protective clothing, in particular gloves, aprons or sleeves, made of the fibrous structure above.

[0017] The fibrous structure of the invention has a high resistance to abrasion. It also has a very high resistance to cutting. With the structure of the invention, it is possible to manufacture high cut and abrasion resistant protective clothing like working gloves. The gloves made of the fibrous structure of the invention are comfortable and, by wearing them, the user does not lose the natural dexterity of his hands.

[0018] The fibrous structure of the invention also finds use in the ballistic area: it has a very good puncture resistance.

[0019] Moreover, since the para-aramid strand of the invention is a non composite one, the manufacturing process of the fibrous structure is very simple and direct and does not require any previous treatment or arrangement of the strand. The manufacturing process can therefore be completed in a minimum number of steps, allowing for a rapid, easy and cost effective realization of any fibrous structure.

DETAILED DESCRIPTION

[0020] "Fibrous structure", as used herein, includes two or three-dimensional structures comprising fibrous material. Preferably, this structure includes knitted fabrics, woven fabrics, unidirectionals, nonwovens, and/or combinations thereof. By "combinations", is meant that structures of different nature and/or construction may be assembled together, either in the same plane or not, as a multilayer structure for instance, by any assembling means like sewing, gluing, stitching and the like. By "nonwovens" is meant fibrous materials combined to a binding matrix of polyethylene, polypropylene, polyamides, phenols, epoxy resins, polyester or mixtures thereof.

[0021] "Fibrous material", as used herein, includes endless fibers such as filaments, short fibrous structures, short cut fibers, microfibers, multifilaments, cords, yarns, fibers, pulps. The fibers may be made into yarns of short fibrous structures which are spun into staple fibers, into yarns of endless fibers or into stretchbroken yarns which can be described as intermediate yarns between staple and continuous yarns.

[0022] "Strand", as used herein, means an ordered assemblage of fibrous material having a high ratio of length to diameter, preferably having a length at least 1000 times its diameter. The strand may be round, flat or may have another cross-sectional shape or it may be a hollow fiber. By "non composite strand", is meant a single simple strand by opposition to assembled strands like cotwisted strands, cotextured strands, intermingled strands, core-spun strands and combinations thereof.

[0023] The structure of the invention comprises at least one non composite para-aramid strand.

[0024] Aramids are polymers that are partially, preponderantly or exclusively composed of aromatic rings, which are connected through carbamide bridges or optionally, in addition, also through other bridging structures. The structure of such aramids may be elucidated by the following general formula of repeating units:

(—NH—Al—NH—CO—A2—CO)n

[0025] wherein A1 and A2 are the same or different and signify aromatic and/or polyaromatic and/or heteroaromatic rings, that may also be substituted. Typically A1 and A2 may independently from each other be selected from 1,4-phenylene, 1,3-phenylene, 1,2-phenylene, 4,4'-biphenylene, 2,6-naphthylene, 1,5-naphthylene, 1,4-naphthylene, phenoxyphenyl-4,4'-diyelen, phenoxyphenyl-3,4'-diylen, 2,5-pyridylene and 2,6-quinolylene which may or may not be substituted by one or more substituents which may comprise halogen, C1-C4-alkyl, phenyl, carboalkoxyl, C1-C4-alkoxyl, acyloxy, nitro, dialkylamino, thioalkyl, carboxyl and sulfonyl. The —CONH—group may also be replaced by a carbonyl-hydrazide (—CONHNH—) group, azo-or azoxygroup.

[0026] These aramids are generally prepared by polymerization of diacid chloride, or the corresponding diacid, and diamine.

[0027] Examples of aramids are poly-m-phenylene-isophthalamide and poly-p-phenylene-terephthalamide.

[0028] Additional suitable aromatic polyamides are of the following structure:

(—NH—Ar—X—Ar2—NH—CO—Ar1—X—Ar2—CO—)n

[0029] in which X represents O, S, SO2, NR, N2, CR2, CO.

[0030] R represents H, C1-C4-alkyl and Ar1 and Ar2 which may be same or different are selected from 1,2-phenylene, 1,3-phenylene and 1,4-phenylene and in which at least one hydrogen atom may be substituted with halogen and/or C1-C4-alkyl.

[0031] Further useful polyamides are disclosed in U.S. Pat. No. 4,670,343 wherein the aramid is a copolyamide in which preferably at least 80% by mole of the total A1 and A2 are 1,4-phenylene and phenoxyphenyl-3,4'-diylene which may or may not be substituted and the content of phenoxyphenyl-3,4'-diylene is 10% to 40% by mole.

[0032] Additives may be used with the aramid and, in fact, it has been found that up to as much as 10% by weight, of other polymeric materials may be blended with the aramid or that copolymers may be used having as much as 10% of other diamine substituted for the diamine of the aramid or as much as 10% of other diacid chloride substituted for the diacid chloride of the aramid.

[0033] The non composite para-aramid strand of the invention preferably has an elongation equal to or less than 5%, measured according to ASTM D885-98. Preferably, the para-aramid strands have a modulus of about 10 to about 2500 g/den, preferably of about 1000 to about 2500 g/den, and a tenacity of about 3 to about 50 g/den, preferably of about 3 to about 38 g/den. The modulus and the tenacity are measured according to the ASTM D 885-98 method.

[0034] The structure of the invention may comprise several para-aramid strands. In such a case, these strands are independent from each other. The para-aramid strands are present in the structure of the invention in an amount ranging from about 20 to about 99.9%, preferably from about 30% to about 70% by weight, relative to the total weight of the structure.

[0035] The strands are generally spun from an anisotropic spin dope using an air gap spinning process such as is well-known and is described in U.S. Pat. Nos. 3,767,756 or 4,340,559.

[0036] The structure of the invention also comprises at least one nylon strand. By "nylon" is meant a strand made from aliphatic polyamide polymers. Suitable nylons in the present invention include polyhexamethylene adipamide (nylon 66), polycaprolactam (nylon 6), polybutyrolactam (nylon 4), poly(9-aminononanoic acid) (nylon 9), polyenantholactam (nylon 7), polycapryllactam (nylon 8) and polyhexamethylene sebacamide (nylon 6,10). Preferred nylon is polyhexamethylene adipamide (nylon 66).

[0037] In a preferred embodiment of the invention, the nylon strand is a textured strand. By "textured strand" is meant a strand which has undergone a treatment, like air-injection for instance, in order to intermingle the originally parallel filaments constituting the strand.

[0038] Preferred nylon strands of the invention have an elongation equal to or less than 18%, and a tenacity equal to or less than 10 gpd. The elongation and the tenacity are measured according to ASTM D885-98.

[0039] Nylon strands are generally spun by extrusion of a melt of the polymer through a capillary into a gaseous congealing medium. Such processes are well-known.

[0040] Suitable nylon strands of the invention include the product sold under the tradename "Cordura®" by E. I. du Pont de Nemours and Company, Delaware.

[0041] The structure of the invention may comprise several nylon strands.

[0042] The non composite para-aramid strand and the nylon strand are maintained in a parallel relationship to each other in the structure of the invention. "Parallel", as used herein, means that the angle between one strand along the entirety of its running length and any other strand along the entirety of its running length is about zero. All the strands remain independent and separate from each other. They are not intimately blended, they are not cotwisted, they are not intermingled, not commingled, not interlaced, not intermixed nor textured. One does not wrap any other one, they do not form a core-spun fiber nor a sheath core.

[0043] In a preferred embodiment of the fibrous structure of the invention, the non composite para-aramid strand is present in an amount ranging from about 30% to about 70% by weight and the nylon strand is present in an amount ranging from about 30% to about 70% by weight, relative to the weight of the structure.

[0044] In addition to the non composite para-aramid strands and the nylon strands described above, the structure of the invention may comprise additional man-made or natural strands. These additional strands include polyethylene strands, polyester strands, acrylic strands, acetate strands, meta-aramid strands, glass strands, steel strands, ceramic strands, polytetrafluoroethylene strands, cellulosic strands, cofton strands, silk strands, wool strands and mixtures thereof. These additional strands may be present in an amount ranging from about 0.25 weight % to about 25 weight %, relative to the total weight of the structure, as long as their presence in the structure of the invention does not negatively impact the specific high abrasion and cut resistance of the structure of the invention. These additional strands are also maintained in a parallel relationship to any other strand present in the structure.

[0045] The structure of the invention shows a very good cut resistance. In a preferred embodiment of the invention, the structure of the invention shows a combined normalized index CTPCPI.N, measured as described below, equal or greater than 80 g/mm, more preferably equal or greater than 90 g/mm. The structure of the invention also shows a very good abrasion resistance. In a preferred embodiment of the invention, the structure shows an abrasion resistance, measured according to EN 388 method, equal or greater than 1000 cycles, more preferably equal or greater than 3000 cycles. In a more preferred embodiment of the invention, the structure shows both a combined normalized index CTPCPI.N, measured as described below, equal or greater than 80 and an abrasion resistance, measured according to EN 388, equal or greater than 1000 cycles.

[0046] The structure of the invention preferably shows a medium weight ranging from about 200 g/m^2 to about 1500 g/m^2, preferably ranging from about 300 g/m^2 to about 800 g/m^2, measured according to EN 388 method.

[0047] The structure of the invention is prepared according to any classical textile process allowing for parallel alignment of the strands making the structure: knitting, weaving, unidirectionally laying down, combining the strands with a binding matrix to form a nonwoven. For instance, in the knitting or weaving process, the strands are fed directly to the knitting machine or the weaving machine without any prior assembly of any sort. For instance, in the knitting process, the order in which the strands are fed into the needles of the knitting machine remains the same during the whole knitting process. Preferred process for making the structure of the invention is the knitting process.

[0048] The structure of the invention may be used in the manufacture of gloves, aprons, sleeves and any protective clothing requiring a high cut resistance and a high abrasion resistance.

[0049] The invention will be explained in more detail with reference to the following examples.

[0050] Test Methods and Examples Description

[0051] Abrasion Resistance

[0052] In the following examples, the abrasion resistance of the samples was measured according to the Standard European Method EN388, July 1994, section untitled "Protective Gloves against Mechanical Risks", subsection 6 "Abrasion resistance".

[0053] The apparatus was the Martindale wear and abrasion tester, designed to give a controlled amount of abrasion between the fabric surface and the selected abradant at relatively low contact pressure of (9+/−0.2) kPa in continuously changing directions. The circular samples were abraded against a standard abrasive glass paper (grade F2 grit 100 quality 117).

[0054] The abrasion was continued and the samples were examined at suitable intervals without removing them from their holder. The rub-through situation was characterized by broken threads and the average values of cycle to reach this breakdown was registered and averaged for 6 samples.

[0055] The test is conducted at (23+/−2) ° C. and (50+/−5) % relative humidity.

[0056] The greater is the number of cycles needed to reach the breakdown, the higher is the resistance to abrasion of the sample.

[0057] Cut Resistance

[0058] In the following examples, the cut resistance was measured according to the "Standard test Method for Measuring Cut Resistance of Materials Used in protective Clothing", ASTM Standard F 1790-97.

[0059] In performance of the test, a cutting edge, under a specified force, was drawn one time across a sample mounted on a cylindrical mandrel. At several different forces, the distance drawn from initial contact to cut through was recorded and a graph was constructed of force as a function of distance to cut through. From the graph, the forces (in grams) were determined to cut through at a distance of 25.4 millimeters, and 10 millimeters, and were normalized to validate the consistency of the blades. These normalized forces are hereinafter respectively referred to as NL1 (for the 25.4 mm distance) and NL2 (for the 10 mm distance). The blades were stainless steel cutter blades with a sharp edge of 70 mm, which were calibrated using a load of 4 N on a neoprene sheet of about (1.57+/−10%) mm and a hardness of (50+/−5) shore A. This was performed at the beginning and at the end of the test. A new blade was used for each measurement, i.e. each load. The sample was a rectangular piece of textile of 50×100 millimeters placed at a biais of 45 degrees. The mandrel was a rounded electroconductive bar with a radius of 38 millimeters and the sample was mounted onto it using double-face tapes. The cutting edge was drawn across the textile on the mandrel at a right angle with the longitudinal axis of the mandrel. Cut through was recorded when the cutting edge makes electrical contact with the mandrel. The normalized forces were reported as the cut resistance forces, respectively NL1 and NL2 expressed in grams for a cut length of 25.4 mm and 10 mm.

[0060] The test is conducted at (23+/−2)° C. and (50+/−5) % relative humidity.

[0061] The 25.4 millimeters cut can be classified as a tear-like-cut and the 10 millimeters cut can be classified as a puncture-like-cut. These two belong to different regions of the cut-length-cut-force relationship, which is a non-linear curve. It was therefore convenient to define a combined index, which has the merit to compound the two behaviors. This index is hereafter referred to as the Combined Tear Puncture Cut Performance Index, CTPCPI. It was computed as per the following equation:

$$CTPCPI = \left[\frac{NL1}{25.4} + \frac{NL2}{10}\right] \Big/ 2 \Leftrightarrow \left[\frac{\text{grams}}{\text{mm}}\right]$$

[0062] This index was further normalized for a constant weight of fabric composition, hereafter selected at 800 grams per square meters. This mass per square area is a realistic value with regard to the protective clothing applications such as gloves for industrial usage.

$$CTPCPI_N = \left\{\left[\frac{NL1}{25.4} + \frac{NL2}{10}\right] \Big/ 2\right\} \times \frac{(800)}{(\text{mass per surface area of the sample})} \Leftrightarrow \left[\frac{\text{grams}}{\text{mm}}\right]$$

[0063] This combined normalized index is given in grams per millimeter of cut length. The higher this index is, the higher is the cut resistance of the sample.

[0064] For each example, 12 samples were tested. The result is the average of the results of the 12 tests.

[0065] Ingredients

[0066] Non composite para-aramid strand A: staple para-aramid yarn of linear density 714dtex, equivalent Nm=28/2 (with dtex=10000/Nm) commercially available from E. I. du Pont de Nemours and Company under the tradename Kevlar® staple aramid fiber, Type 970. The synthetic fiber staples were produced from short para-aramid fibers of 38 mm length as per the state of the art spinning process used for the production of para-aramid staple yarns. The para-aramid short fibers were obtained by cuffing continuous filament para-aramid yarns made of 1000 filaments of 1.5 dpf (1.6dtex) each.

[0067] Nylon strand B: staple yarns of nylon 66 of linear density 370 dtex, equivalent Nm=55/2 (with dtex=10000/Nm), commercially available by E. I. du Pont de Nemours and Company under the trade designation Cordura® Type 200. The synthetic fiber staples were produced from short aliphatic polyamide nylon 66 fibers of 38 mm length as per the state of the art spinning process used for the production of aliphatic polyamide staple yarns. The aliphatic polyamide short fibers were obtained by cutting continuous filament yarns made filaments of 1.9 dtex each.

EXAMPLES

[0068] Examples 1 and 2 are comparative Examples. Example 3 is an example according to the invention. In order for the results to be comparative, all three examples were realized for a relatively constant value of the total dtex (which is representative of the linear density of a fiber) and a relatively constant value of the mass per surface area.

Example 1 Comparative

[0069] Five independent non composite para-aramid strands A were fed to a circular knitting machine (Fiber Analysis Knitter from Lawson-Hamphill) without prior assembling of any sort. A sleeve of sufficient length was knitted to obtain a uniform and reproducible pattern of a mass per surface area close to 800 g/m^2.

[0070] The samples were cut to the adequate dimensions and shapes, circular for the abrasion testing and rectangular for the cut performance measurement, to perform 6 abrasion tests and 12 cut tests.

[0071] Each sample had therefore a total dtex of 3570 (five times 714 dtex).

[0072] The abrasion resistance measured was 900 cycles.

[0073] The forces measured in the cut resistance test were 821 g for a cut length of 25.4 mm and 1666 g for a cut distance of 10 mm. The combined CTPCPI.N normalized index was given by the following calculation [(821/25.4+1666/10)/2]×800/800 and equaled 99 g/mm.

Example 2 Comparative

[0074] Ten independent nylon strands B were fed to the same circular knitting machine as the one used in Example 1 without prior assembling of any sort. A sleeve of sufficient length was knitted to obtain a uniform and reproducible pattern of a mass per surface area close to 826 g/m^2.

[0075] The samples were cut to the adequate dimensions and shapes, circular for the abrasion testing and rectangular for the cut performance measurement, to perform 6 abrasion tests and 12 cut tests.

[0076] Each sample had therefore a total dtex of 3700 (ten times 370 dtex).

[0077] The abrasion resistance measured was 3000 cycles.

[0078] The forces measured in the cut resistance test were 759 g for a cut length of 25.4 mm and 923 g for a cut distance of 10 mm. The combined CTPCPI.N normalized index was given by the following calculation [(759/25.4+923/10)/2]×800/826 and equaled 59 g/mm.

[0079] CTPCPI.N of example 2 reveals an approximate 40% inferior cut resistance compared to example 1. On the other side the abrasion resistance of example 2 is three times superior to the one of example 1.

Example 3

Invention

[0080] Three independent non composite para-aramid strands A and four independent nylon strands B were fed to the same circular knitting machine as the one used in Example 1 without prior assembling of any sort. A sleeve of sufficient length was knitted to obtain a uniform and reproducible pattern of a mass per surface area close to 843 g/m^2.

[0081] The samples were cut to the adequate dimensions and shapes, circular for the abrasion testing and rectangular for the cut performance measurement, to perform 6 abrasion tests and 12 cut tests.

[0082] Each sample had therefore a total dtex of 3622 (three times 714 dtex plus four times 370 dtex). Each sample comprised 50.1% by weight, of non composite para-aramid strand relative to the weight of the sample, and 40.1% by weight, of nylon strand, relative to the weight of the sample.

[0083] The abrasion resistance measured was 6000 cycles.

[0084] The forces measured in the cut resistance test were 1170 g for a cut length of 25.4 mm and 1400 g for a cut distance of 10 mm. The combined CTPCPI.N normalized index was given by the following calculation [(1170/25.4+1400/10)/2]×800/843 and equaled 88 g/mm.

[0085] CTPCPI.N of Example 3 reveals an approximate equal cut resistance compared to Example 1. On the other side, the abrasion resistance of Example 3 is six times superior to the one of Example 1 and surprisingly two times superior to the one of Example 2.

[0086] The following table summarizes the results obtained in Examples 1 to 3.

TABLE I

	Example 1 (comparative)	Example 2 (comparative)	Example 3 (invention)
Total dtex	3570	3700	3622
w % of p-aramid strands	100	0	59
Mass per square area (g/m^2)	800	826	843
CTPCPI.N in g/mm	99	59	88
Abrasion resistance in cycles	900	3000	6000

1. Fibrous structure comprising at least one non composite para-aramid strand and at least one nylon strand maintained in a parallel relationship to each other, the non composite para-aramid strand being present in the structure in an amount ranging from about 20% to 99.9% by weight, relative to the weight of the structure.

2. Structure of claim 1, wherein the non composite para-aramid strand is present in an amount ranging from about 30% to about 70% by weight, and the nylon strand is present in an amount ranging from about 30% to about 70% by weight, relative to the weight of the structure.

3. Structure of claim 1, wherein the nylon strand is a textured strand.

4. Process to manufacture the fibrous structure of claim 1, comprising the step of processing a non composite para-aramid strand and nylon strand in a parallel relationship to each other.

5. Process of claim 4, wherein the processing includes knitting, weaving, unidirectionally laying down or combining the strands with a binding matrix to form a nonwoven.

6. Process of claim 5, wherein processing is knitting.

7. High cut and abrasion resistant protective clothing made of the fibrous structure of claim 1.

8. High cut and abrasion resistant gloves made of the fibrous structure of claim 1.

9. High cut and abrasion resistant sleeve made of the fibrous structure of claim 1.

10. High cut and abrasion resistant apron made of the fibrous structure of claim 1.

11. Process for providing a fibrous structure having high cut and abrasion resistance, comprising:

a) providing strands of at least one non composite para-aramid strand and at least one nylon strand,

b) feeding the strands into a knitting or weaving machine without prior assembly,

c) knitting or weaving a fibrous structure without changing the order in which the strands are fed into the machine, the strands being maintained in a parallel relationship to each other during the whole knitting or weaving process.

12. Structure of claim 1, showing a combined normalized index CTPCPI.N, equal or greater than 80 g/mm and an abrasion resistance, measured according to EN 388, equal or greater than 1000 cycles.

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