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(54) Title: ADVANCED ANTIBALLISTIC MATERIALS

(57) Abstract: A stack is proposed comprising at least one layer of tapes and at least one layer of multifilament yarn.

Advanced Antiballistic Materials

Description:

The invention pertains a stack comprising at least one layer of multifilament yarns, in particular for anti ballistic applications. Combinations wherein layers of multifilament yarns are used to achieve anti ballistic performances are known e.g. from US 2005/0153098. This publication describes stacked layers in the form of a crossply of layers of multifilament yarns. In order to protect the filaments from deterioration by rubbing or in use PET and PC films on the outside of this stack are applied.

Although the stacked layers of multifilament yarns of the prior art show good antiballistic performances, their cost-prices are often very high and also the processes of manufacturing the required yarns are complicated and both time and cost consuming.

As a consequence, there is a need for alternatives that are cheaper and easier to manufacture and which alternatives still have properties that enables them for antiballistic applications.

Surprisingly, the object of the invention can be achieved with a stack of at least one layer of multifilament yarns and at least one layer of tapes.

Throughout this description, the term "multifilament yarns", also referred to below simply as "yarns", refers to linear structures consisting of two or more filaments of in principle endless length. Such multifilaments are known to the skilled person. There is in principle no restriction on the number of individual filaments comprising

a multifilament yarn. A multifilament generally comprises between 10 and 500 filaments, and frequently between 50 and 300 filaments.

Multifilament yarns for anti ballistic applications are usually yarns from the ultra high molecular weight polyethylene (UHMWPE) or aramid (poly paraphenylene terephthalamide) type, however, also other high performance fibers as mentioned below can be applied.

In the course of this invention a “layer of multifilament yarns” should be understood as one layer of (spread) multifilament yarns in one direction.

Under the term “crossply” at least two layers are to be understood, which layers have directions deviating from each other in an angle from 0 to 90 °, i.e. the layers are not parallel to each other.

Further, with the term “laminate” a combination of at least two crossplies in a flexible manner is meant, such as combining two or more crossplies by means of e.g. sewing. In contrast to that, with the term “panel” or “plate” combinations of two or more crossplies in a rigid manner is meant, which can be achieved e.g. by applying pressure and temperature to the stack of crossplies.

With the term “tape” a highly drawn slitted film, an extruded mono-polymer, or bicomponent extruded drawn slitted films or co-extruded multilayer “monofilament”, a so called SSE (solid state extruded) highly drawn film known as e.g. Tensylon, Pamaco and other equivalents is meant. Important is a tape strength between 50 cN /tex and 500cN/tex and a “thickness to width” ratio between 1:2 and 1: 100.000, preferably between 1:10 and 1:10000. Examples of suitable tapes are disclosed in WO 2006/107197 and in applicant’s unpublished applications No. PCT/EP2007/008495, PCT/EP2007/008500, PCT/EP2007/008499, and PCT/EP2007/008498.

With “UD-0” (uni-directional with an angle of 0°) one layer of plane parallel positioned tapes is meant, e.g. positioned next to each other (shoulder to shoulder or side by side).

A layer of “UD-brick” consists of two layers of “UD-0” parallel positioned above each other with an offset of ca. 50 % of the width of the tape.

Accordingly, a UD-brick crossply is a 0-90 degree stack of at least two layers of UD-bricks which layers have directions deviating from each other in an angle from 0 to 90 °, i.e. the layers are not parallel to each other.

For the tapes preferably polymers, such as PP, PE, HDPE, PET, PA, PPS, PBO, HDPP, UHMWPE, UHMWPP, HDPA, UHMWPA are used. The most common polymers for these tapes are polyethylene, polypropylene, PET (Polyethylene terephthalate), PEN (Polyethylene Naphthalate), Polyamide, PPS and/or mixtures thereof.

In the course of the invention, HDPE can be defined as drawn polyethylene with a molecular weight of less than 1.000.000, preferably produced by meltspinning.

UHMWPE can be defined as polyethylene with a molecular weight of more than 1.000.000.

The invention is to supply stack of layers of multifilaments yarns and tapes in all possible combinations.

Preferably the inventive stack comprises more than two individual layers.

In a preferred embodiment the stack comprises one individual layer of tape, then a layer of multifilament yarns, and again a layer of tapes, i.e. alternating layers of tapes and multifilament yarns.

In a further preferred embodiment the stack of the invention comprises a small number of one kind of layers of tape, followed by a small number of layers of one or more kinds of multifilament yarns. In the framework of the present invention the term “small number of layers” should be understood as 2 to 20 layers, preferably 3 to 15 layers and more preferably 5 to 10 layers. The small number of tape layers may be different from the small number of multifilament layers. Preferably there are equal numbers of tape layers and multifilament yarn layers.

Combinations of the embodiments described above are also encompassed.

The tape layer can be present in its UD-0 form or as UD-brick. Both the layer(s) of multifilament yarns and the layer(s) of tape can be present as double- and/or multilayer crossply.

The layers of multifilament yarns can consist of the family of para-aramid multifilament yarns, known and sold under the trade names like e.g. Twaron, Kevlar, Heracron, Pycap or Artec, high strength polyethylene multifilament yarns like Dyneema, Spectra or the various Chinese UHMWPE multifilament yarns, high strength glass multifilament yarns known as E-glass, R-glass and S-glass.

Furthermore other high performance multifilament yarns like carbon multifilament yarns, HS basalt multifilament yarns; polybenzoxazole (PBZO) multifilament yarns, polybenzothiazole (PBZT) multifilament yarns, HDPA multifilament yarns, UHMWPA multifilament yarns, UHMWPP multifilament yarns, HDPP multifilament yarns, HDPE multifilament yarns etc; basically any multifilament high strength yarn with a strength above 60 cN/tex as they are in use in this anti-ballistic and “life protection” industry or composite industry can be applied.

It is preferred though, that the single filaments have a small diameter, preferably between 3 microns and 50 microns (μm), even more preferably between 5 and 30 microns. Also, one or more combinations of these multifilament yarns can be used together in one or more of the layers of multifilament yarns.

One aspect of the stack according to the invention is the relatively low adhesion between and/or within the various layers, caused by a low adhesive or resin content in the layers. Preferred are adhesive contents between 2 % and 30 %, more preferably between 5 and 12 %, of the weight of the total stack, leaving – even under high pressures and heat, e.g. a pressure of five MPa or more and a temperature of 100 °C or more during the manufacturing of the crossply, laminate or panel – some or better most filaments “un-bonded” within the stack.

Preferred adhesives or resins are e.g. latices of Kraton, PU, Acrylics , but also dispersions of EAA, EMA, EVA ,OBC (Olefin Block Copolymer) (Infuse ® DOW) etc. or various solvent based/water based adhesives with chloroprene and alike. Further suitable adhesives may be selected from the group consisting of polyethylene, ultra high molecular weight polyethylene, polypropylene, polyamide, polybutadiene terephthalate and polyethylene terephthalate, polyethylene naphtalate, polyvinyl alcohol, polyphenylidensulfide, copolymers of these polymers and mixtures thereof. In addition ethylene alkyl acrylate copolymer (EAA), ethylene vinyl acetate copolymer (EVA), ethylene-butyl acrylate copolymer (EBA), ethylenemethyl acrylate copolymer (EMA), linear low density polyethylene (LLDPE), high density polyethylenes (HDPE), low density polyethylenes (LPDE) may be used. It is also possible to use polyisobutylene (PIB) or polyurethane (PU) and mixtures thereof. The adhesive or resin material may comprise one of the listed materials or mixtures of those materials.

The volume ratio of the layers of multifilament yarns and the layers of tapes should be between 1: 99 % and 99:1 %, preferably between 30:70 and 70:30 , most preferably between 33:67 % and 67:33 %, this depending on the desired ballistic performance and the allowed maximum weight and of course the cost per unit.

Further preferred embodiments of the present inventions are the following stacks, which can finally become crossplies, laminates or panels.

A stack which comprises at least one layer of HDPE-tapes and at least one layer of aramid multifilament yarns.

A stack which comprises at least one layer of HDPE-tapes and at least one layer of UHMWPE multifilament yarns.

A stack which comprises at least one layer of UHMWPE-tapes and at least one layer of aramid multifilament yarns.

A stack which comprises at least one layer of HDPE-tapes and at least one layer of aramid multifilament yarns and at least one layer of UHMWPE multifilament yarns.

A stack which comprises at least one layer of UHMWPE-tapes and at least one layer of aramid multifilament yarns and at least one layer of UHMWPE multifilament yarns.

A stack which comprises at least one layer of HDPE-tapes and at least one layer of basalt multifilament yarns.

A stack which comprises at least one layer of UHMWPE-tapes and at least one layer of basalt multifilament yarns.

The stacks of the present invention as well as the resulting panels or laminates exhibit performance improvement and/or cost improvement over the prior art materials since tapes, in particular meltspun but also others, can be produced at lower costs than multifilament yarns.

The stacks according to the invention and the resulting laminates and panels can be applied in antiballistic applications as well as in composite applications, stand-alone or in combination with other materials. Laminates can be used for soft ballistic applications, e.g. vests and so on.

The panels can be used for hard ballistics purposes like panel in cars or trucks, inserts and so on. These panels can also be used behind a hard strike surface, from e.g. metals, metal alloys, glass basalt fibers, glass fibers, and ceramics, e.g. aluminum oxide, boron carbide.

Two or more hard strike surface layers (e.g. from ceramic or steel) can also be combined with two or more of the panels, such as e.g. sandwiching the hard strike surface layers by the panels.

The low adhesive content in the stack according to the invention, which has by nature a relatively high specific surface due to the many very small diameter filaments, in combination with the relatively small specific surface of the tapes, helps to absorb energy by delamination upon impact. The multifilament yarns and tapes separate from each other when hit by e.g. a bullet which enables the energy to be absorbed and dissipated.

A possible variation is to connect the layers to each other by surface-fusing of the material within the stack with the lowest melting temperature to achieve a bonding of the layers in the stack.

The high performance multifilament yarns like UHMWPE and para aramid tend to be more expensive than e.g. the highly drawn slitted film tapes, thus in certain "low cost" applications the ratio will be in favor of the higher tape-layer content, reducing the over-all price of the stack and the resulting panel or laminate.

The mechanical performances of the HDPE tapes with a tensile strength of 1700 MPa (as shown in the example below) are lower than the mechanical properties of the multifilament yarns like Aramid (with 2800 MPa). However, similar or nearly similar anti ballistic effects can be realized as with the materials of the prior consisting of 100 % of multifilament yarns.

EXAMPLE

A panel of a 50/50 ratio by weight of layers of HDPE UD-brick tape and crossplies from (spread) aramid multifilament yarns can withstand nearly similar impact energy of a bullet as an equally heavy all-aramid multifilament yarn panel, due to the slippage effect and favorable energy dissipation of the panel.

The stack was constructed as follows:

Stack:

Adhesive 4 µm

HDPE UD-brick (80 gr layer, 35 µm HDPE 0°, 8 µm adhesive, 35 µm HDPE 0°)

Adhesive 4 µm

Aramid 90-0 (80 gr layer, 38 gr aramid 90°, 4 µm adhesive, 38 gr aramid 0°)

Adhesive 4 µm

HDPE UD-brick (80gr layer, 35µm HDPE 90°, 8 µm foil, 35 µm HDPE 90°)

Adhesive 4 µm

Aramid 0-90 (80 gr layer, 38 gr Aramid 0°, 4 µm adhesive, 38 gr Aramid 90°)

Advanced Antiballistic Materials

Claims:

- 1) A stack of at least one layer of tapes and at least one layer of multifilament yarn, wherein the stack comprises a small number of one kind of layers of tape, followed by a small number of layers of one or more kinds of multifilament yarns and wherein the tapes are HDPE tapes or UHMWPE tapes.
- 2) The stack of claim 1, wherein the multifilament yarns consist of ultra high molecular weight polyethylene or aramid polymer.
- 3) The stack of claims 1 or 2, wherein the tapes consist of a highly drawn slitted film, an extruded mono-polymer, or bicomponent extruded drawn slitted films or co-extruded multilayer monofilament.
- 4) The stack of any of the preceding claims, wherein the polymers for the tapes are selected from a group consisting of polyethylene, polypropylene, PET (Polyethylene terephthalate), PEN (Polyethylene Naphthalate), Polyamide, PPS and/or mixtures thereof.
- 5) The stack of any of the preceding claims, wherein the stack comprises one individual layer of tape, then a layer of multifilament yarns, and again a layer of tapes.
- 6) The stack of any of the preceding claims, wherein the layer of tapes is present in its UD-0 form.

- 7) The stack of any of the preceding claims, wherein the layer of tapes is present in its UD-brick form.
- 8) The stack of any of the preceding claims, wherein both the layer(s) of multifilament yarns and the layer(s) of tape are present as double- and/or multilayer crossply.
- 9) The stack of any of the preceding claims, wherein layers of multifilament yarns consist of para-aramid multifilament yarns, selected from a group consisting of Twaron, Kevlar, Heracron, Pycap or Artec, high strength polyethylene multifilament yarns like Dyneema, Spectra or the various Chinese UHMWPE multifilament yarns, high strength glass multifilament yarns known as E-glass, R-glass and S-glass, carbon multifilament yarns, HS basalt multifilament yarns; polybenzoxazole (PBZO) multifilament yarns, polybenzothiazole (PBZT) multifilament yarns, HDPA multifilament yarns, UHMWPA multifilament yarns, UHMWPP multifilament yarns, HDPP multifilament yarns, HDPE multifilament yarns.
- 10) The stack of any of the preceding claims, wherein the multifilament yarns have a strength above 60 cN/tex.
- 11) The stack of any of the preceding claims, wherein the diameter of the single filaments of the multifilament yarns is between 3 and 50, preferably between 5 and 30 microns (μm).
- 12) The stack of any of the preceding claims, wherein the stack exhibits an adhesive content between 2 % and 30 %, preferably between 5 and 12 %, of the weight of the total stack.
- 13) The stack of claim 12, wherein the adhesives are selected from a group consisting of latices of Kraton, PU, Acrylics, dispersions of EAA, EMA, EVA, OBC (Olefin Block Copolymer) (Infuse R DOW) or various solvent based/water based adhesives with chloroprene and alike, polyethylene, ultra high molecular weight polyethylene, polypropylene, polyamide,

polybutadiene terephthalate and polyethylene terephthalate, polyethylene naphtalate, polyvinyl alcohol, polyphenylidensulfide, alkyl acrylate copolymer (EAA), ethylene vinyl acetate copolymer (EVA), ethylene-butyl acrylate copolymer (EBA), ethylenemethyl acrylate copolymer (EMA), linear low density polyethylene (LLDPE), high density polyethylenes (HDPE), low density polyethylenes (LPDE), polyisobutylene (PIB) or polyurethane (PU), copolymers of these polymers and/or mixtures thereof.

- 14) The stack of any of the preceding claims, wherein the volume ratio of the layers of multifilament yarns and the layers of tapes is between 1: 99 % and 99:1 %, preferably between 30:70 and 70:30.
- 15) The stack of any of the preceding claims, comprising at least one layer of HDPE-tapes and at least one layer of aramid multifilament yarns.
- 16) The stack of any of the preceding claims, comprising at least one layer of HDPE-tapes and at least one layer of UHMWPE multifilament yarns.
- 17) The stack of any of the preceding claims, comprising at least one layer of UHMWPE-tapes and at least one layer of aramid multifilament yarns.
- 18) The stack of any of the preceding claims, comprising at least one layer of HDPE-tapes and at least one layer of aramid multifilament yarns and at least one layer of UHMWPE multifilament yarns.
- 19) The stack of any of the preceding claims, comprising at least one layer of UHMWPE-tapes and at least one layer of aramid multifilament yarns and at least one layer of UHMWPE multifilament yarns.
- 20) The stack of any of the preceding claims, comprising at least one layer of HDPE-tapes and at least one layer of basalt multifilament yarns.
- 21) The stack of any of the preceding claims, comprising at least one layer of UHMWPE-tapes and at least one layer of basalt multifilament yarns.
- 22) The stack according to any of claims 1 to 21, wherein the layers are connected to each other by surface-fusing of the material within the stack

with the lowest melting temperature to achieve a bonding of the layers in the stack.

- 23)A crossply comprising a stack according to any of the preceding claims 1 to 22.
- 24)A laminate comprising a stack according to any of the preceding claims 1 to 23.
- 25)A panel comprising a stack according to any of the preceding claims 1 to 24.
- 26)Use of the laminates according to claim 24 for soft antiballistic applications such as vests.
- 27)Use of the panel according to claim 25 for hard antiballistics purposes, where a rigid plate or panel is required.
- 28)Use of the panel according to claim 25 for composite purposes.
- 29)Use of the panel according to claim 25 behind a hard strike surface, from e.g. metals, metal alloys, glass basalt fibers, glass fibers, and ceramics, e.g. aluminum oxide, boron carbide and silicon carbide.
- 30)Use of two or more of the the panel according to claim 25 in combination with Two or more hard strike surface layers.

INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER
INV. B32B3/10 B32B5/02 F41H5/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B32B F41H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 677 029 A (PREVORSEK DUSAN C [US] ET AL) 14 October 1997 (1997-10-14) column 1, lines 10-12 column 1, line 66 - column 2, line 5 column 11, lines 50-54 column 11, line 66 - column 12, line 6 column 5, lines 23-32	1-30
X	WO 2006/136323 A (TEIJIN TWARON GMBH [DE]; PROPEX FABRICS GMBH [DE]; BOETTGER CHRISTIAN) 28 December 2006 (2006-12-28) claims 1,8 example 5	1-30
A	EP 0 805 332 A (CITTERIO S P A FLLI [IT]) 5 November 1997 (1997-11-05) claim 1	-/-

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
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X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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Date of the actual completion of the international search	Date of mailing of the international search report
23 December 2008	13/01/2009
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Schambeck, Werner

INTERNATIONAL SEARCH REPORT

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 309 487 A (HOLMES RICHARD R) 5 January 1982 (1982-01-05) Claim 1 -----	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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