Abstract: The present invention pertains to a ballistic-resistant article comprising a stack of sheets comprising reinforcing linear tension members, the direction of the linear tension members within the stack being not unidirectionally, wherein some of the linear tension members are linear tension members comprising high molecular weight polyethylene and some of the linear tension members comprise aramid. It is preferred for the polyethylene linear tension members to be tapes. In one embodiment, the stack comprises a layer which comprises more than 50 wt.% of polyethylene linear tension members and a layer which comprises more than 50 wt.% of aramid linear tension members.
Ballistic-resistant articles

The present invention pertains to ballistic-resistant articles, to sheets suitable for use in the manufacture of ballistic-resistant articles, to a consolidated sheet package, and to a method for manufacturing a ballistic-resistant article.

Ballistic-resistant articles are known in the art. They are available in numerous different kinds. On the one hand, there exist soft-ballistic articles, for example for use in bullet-proof vests. On the other, there exist moulded bodies, serving, for example, as shields in another type of bullet-proof vests, or as helmets. Further, ballistic-resistant articles are used in cars, buildings, and other objects intended to help to protect, people, animals, or goods from ballistic impact.

In the art, ballistic-resistant articles often comprise a stack of sheets containing high-strength fibers, such as aramid, or polyethylene. Depending on the application, the sheets may be pressed together to form a moulded article, or bonded together at the edges to form a soft-ballistic article. There is need for a ballistic-resistant article with improved properties.

The use of different materials in antiballistic panels has been suggested.

WO2005098343 describes an armour system with a hardened strike panel and a backing panel. Materials mentioned to be suitable for the strike panel include granite, ceramic tile, brick, glass and hardened concrete. On the other hand some of the materials mentioned to be suitable for the packing panel
include glass, aramid, polyethylene, carbon and metallic materials.

WO2008048301 is directed to a composite material for forming a flexible bullet-resistant body armor comprising at least one fibrous layer comprising a network of high tenacity fibers. The high tenacity fibers may be PE fibers and aramid fibers among at least 8 other type of fibers. This document generally mentions that the yarns and fabrics of the invention may be comprised of one or more different fibers, although it is preferred that they are the same.

It has been found that substantial improvement in the performance of ballistic materials may be obtained if a combination of two types of high-performance material is used, viz. on the one hand aramid material and on the other high molecular weight polyethylene. Accordingly, the present invention pertains to a ballistic-resistant article comprising a stack of sheets comprising reinforcing linear tension members, the direction of the linear tension members within the stack being not unidirectionally, wherein some of the linear tension members are linear tension members comprising high molecular weight polyethylene and some of the linear tension members comprise aramid.

The linear tension members

Within the context of the present specification the wording linear tension member refers to an object the largest dimension of which, the length, is larger than the second smallest dimension, the width, and the smallest dimension, the thickness. More in particular, the ratio between the length and the width generally is at least 10. The maximum ratio is not critical to the present invention and will depend on
processing parameters. As a general value, a maximum length to width ratio of 1 000 000 may be mentioned. Accordingly, the linear tension members used in the present invention encompass monofilaments, multifilament yarns, threads, tapes, strips, staple fibre yarns and other elongate objects having a regular or irregular cross-section. In one embodiment of the present invention, the linear tension member is a fibre, that is, an object of which the length is larger than the width and the thickness, while the width and the thickness are within the same size range. More in particular, the ratio between the width and the thickness generally is in the range of 10:1 to 1:1, still more in particular between 5:1 and 1:1, still more in particular between 3:1 and 1:1. As the skilled person will understand, the fibres may have a more or less circular cross-section. In this case, the width is the largest dimension of the cross-section, while the thickness is the shortest dimension of the cross section.

For fibres, the width and the thickness are generally at least 1 micron, more in particular at least 7 micron. In the case of multifilament yarns the width and the thickness may be quite large, e.g., up to 2 mm. For monofilament yarns a width and thickness of up to 150 micron may be more conventional. As a particular example, fibres with a width and thickness in the range of 7-50 microns may be mentioned.

In the present invention, a tape is defined as an object of which the length, i.e., the largest dimension of the object, is larger than the width, the second smallest dimension of the object, and the thickness, i.e., the smallest dimension of the object, while the width is in turn larger than the thickness. More in particular, the ratio between the length and the width generally is at least 2. Depending on tape width and stack size the ratio may be larger, e.g., at least 4, or at least 6. The maximum ratio is not critical to the present invention and
will depend on processing parameters. As a general value, a maximum length to width ratio of 200,000 may be mentioned. The ratio between the width and the thickness generally is more than 10:1, in particular more than 50:1, still more in particular more than 100:1. The maximum ratio between the width and the thickness is not critical to the present invention. It generally is at most 2000:1.

The width of the tape generally is at least 1 mm, more in particular at least 2 mm, still more in particular at least 5 mm, more in particular at least 10 mm, even more in particular at least 20 mm, even more in particular at least 40 mm. The width of the tape is generally at most 200 mm. The thickness of the tape is generally at least 8 microns, in particular at least 10 microns. The thickness of the tape is generally at most 150 microns, more in particular at most 100 microns. In one embodiment, tapes are used with a high linear density. In the present specification the linear density is expressed in dtex. This is the weight in grams of 10,000 metres of film. In one embodiment, tapes are used with a linear density of at least 3000 dtex, in particular at least 5000 dtex, more in particular at least 10,000 dtex, even more in particular at least 15,000 dtex, or even at least 20,000 dtex.

The use of tapes has been found to be particularly attractive within the present invention because it enables the manufacture of ballistic materials with very good ballistic performance, good peel strength, and low areal weight. This goes in particular for polyethylene.

Where in the present specification mention is made of weight percentages of linear tension members, this always intends to refer to the high-strength constituent of such member, viz., the polyethylene, aramid, or other high-strength polymer. Any
coatings or finishing present on the linear tension member is calculated to belong to the matrix material.

The composition of the stack

The stack according to the invention comprises sheets comprising linear tension members. Within the present specification, the term sheet refers to an individual sheet comprising linear tension members, which sheet can individually be combined with other, corresponding sheets. The sheet may or may not comprise a matrix material, as will be elucidated below.

The sheets comprising the linear tension members used in the stack according to the invention may be compositioned in different manners.

In one embodiment, sheets are prepared by weaving of linear tension members. In one embodiment, tapes used as warp and weft. In another embodiment, tapes are used as warp or weft, and fibers are used as weft or warp. In a further embodiment, fibers are used as both warp and weft. Weaving may be used to manufacture sheets which contain polyethylene and not aramid, e.g. polyethylene only, and sheets which contain aramid and not polyethylene, e.g., aramid only. It may also be used to manufacture sheets which contain both linear tension members comprising aramid and linear tension members comprising polyethylene. In one embodiment the woven sheet comprises one of polyethylene and aramid linear tension members as warp or weft and the other of polyethylene and aramid linear tension members as weft or warp. It is also possible to use a combination of aramid linear tension members and polyethylene linear tension members in the warp, or in the weft, or both in the warp and in the weft.
It is also possible to use linear tension members which comprise both aramid and polyethylene in the woven sheet.

Various conventional weaving methods may be applied. The weft member can cross over one, two, or more warp members, and the sequential weft members can be applied alternating or parallel. One embodiment in this respect is the plain weave, wherein the warp and weft are aligned so that they form a simple criss-cross pattern. It is made by passing each weft member over and under each warp member, with each row alternating, producing a high number of intersections. A further embodiment is based on the satin weave. In this embodiment, two or more weft members float over a warp member, or vice versa, two or more warp members float over a single weft member. A still further embodiment is derived from the twill weave. In this embodiment, one or more warp members alternately weave over and under two or more weft members in a regular repeated manner. This produces the visual effect of a straight or broken diagonal ‘rib’ to the fabric. A still further embodiment is based on the basket weave. Basket weave is fundamentally the same as plain weave except that two or more warp fibres alternately interlace with two or more weft fibres. An arrangement of two warps crossing two wefts is designated 2x2 basket, but the arrangement of fibre need not be symmetrical. Therefore it is possible to have 8x2, 5x4, etc. A still further embodiment is based on the mock leno weave. Mock leno weave is a version of plain weave in which occasional warp members, at regular intervals but usually several members apart, deviate from the alternate under-over interlacing and instead interlace every two or more members. This happens with similar frequency in the weft direction, and the overall effect is a fabric with increased thickness, rougher surface, and additional porosity.
Each weave type has associated characteristics. For example, where a system is used in which the weft crosses one, or a small number, of warp members, and the individual weft members are used alternating, or almost alternating, the sheet will contain a relatively large number of intersections. An intersection, in this context, is a point where a weft member goes from one side of the sheet, the A side, to the other side of the sheet, the B side and an adjacent weft member goes from the B side to the A side of the sheet. Where a system is used in which the weft crosses one, or a limited number of warp members, or vice versa, where the warp crosses one or a limited number of weft members, a large number of deflection lines will exist. Deflection lines occur where one member goes from one side of the sheet to the other side. It is formed by the edge of the crossover member. While not wishing to be bound by any theory it is believed that these deflection lines contribute to the dissipation of impact energy in the X-Y direction of the sheet. Within the context of the present invention the use of plain weaves may be preferred, because they are relatively easy to manufacture, and because they are homogeneous in that a rotation of 90° will not change the nature of the material, combined with good ballistic performance.

Suitable weaving processes are known in the art. To mention but one example, for an attractive tape weaving process, reference is made to EP 1354991.

In one embodiment of the present invention the linear tension members in a sheet are unidirectionally oriented, and the direction of the linear tension members in a sheet is rotated with respect to the direction of the linear tension members of other sheets in the stack, more in particular with respect to the direction of the linear tension members in adjacent sheets. Good results are achieved when the total rotation
within the stack amounts to at least 45 degrees. Preferably, the total rotation within the stack amounts to approximately 90 degrees. In one embodiment of the present invention, the stack comprises adjacent sheets wherein the direction of the linear tension members in one sheet is perpendicular to the direction of linear tension members in adjacent sheets. In this embodiment, a sheet may be provided by parallel aligning of linear tension members, and then causing the linear tension members to adhere, for example by temperature and pressure, or by using a matrix material. In one embodiment, where the linear tension members are fibers, a sheet may be manufactured by parallel aligning of the fibers, and then providing a matrix material on an between the fibers in an amount sufficient to cause the fibers to adhere.

Where the linear tension members are tapes, there are a number of possibilities to prepare suitable sheets by parallel alignment of tapes. In one embodiment, a single layer of parallel tapes is provided which are then adhered to each other using a matrix material, analogous to what has been described above for fibers. In another embodiment, a sheet is provided by provision of parallel tapes in an overlapping fashion, and then causing the tapes to adhere to each other. In one embodiment, tapes are aligned in such a manner that a first longitudinal edge of the tape is below the tape adjacent on one side and the second longitudinal edge of the tape is above the adjacent tape on the other side (roof-tiling construction). In another embodiment, tapes are aligned in brick-layering fashion, wherein in a first step a first layer of parallel tapes is provided, and in a second step a second layer of tapes is provided, parallel to the tapes in the first layer, wherein the tapes in the second layer are off-set as compared to the tapes in the first layer. If so desired, third and further
layers of tapes may be provided. The tapes are then integrated to form a sheet using temperature and pressure, by using a matrix material or by a combination thereof.

It is also possible to manufacture a sheet by first providing a layer of tapes or fibers aligned in a first direction, then providing a layer of tapes or fibers aligned in a second direction at an angle to the first direction, and then adhering the layers together to form a sheet.

If so desired, fibers and tapes may be used in combination in a single sheet. In one embodiment the sheet contains polyethylene linear tension members and not aramid linear tension members. In another embodiment, the sheet contains aramid linear tension members and not polyethylene linear tension members. In a further embodiment, the sheet comprises both aramid linear tension members and polyethylene linear tension members. It is again also possible to use linear tension members which contain both aramid and polyethylene.

As indicated above, it is a key feature of the ballistic-resistant article of the present invention that some of the linear tension members are linear tension members comprising molecular weight polyethylene and some of the linear tension members comprise aramid. Obviously in addition to linear tension members of polyethylene alone, or aramid alone, the present invention also encompasses the use of linear tension members containing both aramid and polyethylene. The use of hydrid fibers may be mentioned as an example.

The ballistic-resistant article of the present invention may comprise additional types of high-performance linear tension members, e.g., linear tension members of liquid crystalline polymer, and of highly oriented polymers such as polyesters, polyvinylalcohols, polyolef ineketone (POK), polybenzobisoxazoles, polybenz (obis) imidazoles, poly{2,6-
diimidazo \[4,5-b:4,5-e\] -pyridinylene-1, 4 (2, 5-
dihydroxy) phenylene \} (PIPD or M5) and polyacrylonitrile. However, to keep the system as simple as possible it is considered preferred for the linear tension members in the ballistic-resistant article to be for at least 80 wt.% made up from of the total of aramid and polyethylene, in particular for at least 90 wt.%, more in particular for at least 95 wt.%. In one embodiment, the linear tension members in the ballistic-resistant article are essentially of aramid material and polyethylene.

Generally, of the total weight of linear tension members used, the weight percentage of aramid is at least 1%, more in particular at least 5%, even more in particular at least 10%, yet more in particular at least 15%, still more in particular at least 20%. The weight percentage of aramid linear tension members is generally at most 60%, more in particular at most 50%, still more in particular at most 40%. In one embodiment the weight percentage of aramid is between 1 and 20 wt.% of the total weight of linear tension members used in the stack, more specifically between 1 and 10 wt.%, the balance preferably being UHMWPE. In another embodiment the weight percentage of aramid is between 15 and 40 wt.%, in particular between 15 and 30 wt.%, the balance preferably being UHMWPE.

Generally, of the total weight of linear tension members used, the weight percentage of UHMWPE is at least 10%, more in particular at least 15%, still more in particular at least 20%. In one embodiment, the weight percentage of UHMWPE members may be at least 40%, at least 50%, or even at least 60%, in particular at least 80%, more in particular at least 90%, even more in particular at least 95%. Generally, the weight percentage of polyethylene will be at most 99.

The distribution of the aramid and polyethylene linear tension members through the stack may be performed in different
manners. In one embodiment, the stack comprises sheets which contain both polyethylene linear tension members and aramid linear tension members. In another embodiment the stack comprises sheets which comprise polyethylene linear tension members and are free of aramid linear tension members and/or sheets which comprise aramid linear tension members and are free of polyethylene linear tension members.

In one embodiment, the polyethylene linear tension members and aramid linear tension members are distributed homogeneously over the thickness of the stack. That is, when the stack is split along a plane parallel to the plane of the stack, the composition of the two - or more - parts thus obtained is the same.

In another embodiment, the polyethylene linear tension members and aramid linear tension members are distributed inhomogeneously over the thickness of the stack. That is, when the stack is split along a plane parallel to the plane of the stack, the composition of the two - or more - parts thus obtained is different.

In one embodiment, the stack, or the moulded panel derived from the stack by compressing the sheets together, comprises layers with different compositions, wherein each layer can consist of one or more sheets. For example, the stack can comprise two layers, three layers, or more layers, wherein the layers have different compositions from the layers adjacent thereto. Each layer may comprise a combination of polyethylene-based sheets and aramid-based sheets, but may also be a polyethylene-only layer or an aramid-only layer.

In one embodiment, the article comprises a layer which comprises more than 50 wt.% of polyethylene linear tension members and a layer which comprises more than 50 wt.% of
aramid linear tension members. For example the polyethylene-rich layer may generally comprise more than 50 wt.% of polyethylene-based sheets and less than 50 wt.% of aramid-based sheets.

In one embodiment, the layer which comprises more than 50 wt.% of polyethylene linear tension members, further also indicated as the polyethylene-rich layer, comprises more than 60% of said members, or more than 70% of said members, or more than 80%, or more than 90%, or more than 95%. In one embodiment, said layer consists essentially of polyethylene linear tension members.

The polyethylene-rich layer is preferably present at or near the strike face of the article, preferably at the strike face of a moulded panel, where it can serve to fragment the bullet.

In one embodiment, the layer which comprises more than 50 wt.% of aramid linear tension members, further also indicated as aramid-rich layer, comprises more than 60% of said members, or more than 70% of said members, or more than 80%, or more than 90%. In one embodiment, said layer consists essentially of aramid linear tension members. In one embodiment this layer is present below (from the strike side) the polyethylene-rich layer. In this embodiment, the aramid-rich layer may serve to catch the bullet fragments, and/or to reduce trauma. The aramid layer further contributes to preserving the integrity of the panel upon bullet impact.

It is to be noted that in this paragraph, and in the rest of the specification unless indicated otherwise, weight percentages of one type of linear tension member are weight percentages calculated on the total of linear tension members in the layer, excluding matrix material. Thus, layers consisting essentially of polyethylene linear tension members or aramid linear tension members may comprise matrix material.
In one embodiment, an aramid-rich layer as specified above is present at the top of the article, especially in the case of moulded articles such as shields, or, in particular, helmets. This layer may serve to provide increased hardness to the article and to improve its fire resistance. In this embodiment a stack of - at least - three layers may be preferred, wherein the top layer is an aramid-rich layer, the second layer is a polyethylene-rich layer, and the third layer is again an aramid-rich layer.

In a further embodiment, a stack is envisaged which comprises, from the strike face down, a polyethylene-rich layer, and a layer comprising equal amounts of polyethylene and aramid. This may optionally be combined with one or more aramid-rich layers, which may contain different amounts of aramid.

In a further embodiment, a stack is envisaged which comprises at least two polyethylene-rich layers, wherein the first polyethylene-rich layer has a higher polyethylene content than the second layer. The first polyethylene-rich layer may be closer to the strike face of the stack than the second layer. Alternatively, the second layer (i.e. the layer with a lower polyethylene content) may be closer to the strike face of the stack. This may optionally be combined with one or more polyethylene-rich layers and/or aramid-rich layers, which may contain different amounts of polyethylene or aramid respectively.

In general, the stack will comprise 10-99 wt.%, in particular 10-90 wt.% of polyethylene rich layers, calculated on the total stack, and 1-90 wt.%, in particular 10-90 wt.% of aramid-rich layers, calculated on the total stack.

In one embodiment, the stack comprises at least 30 wt.% of polyethylene-rich layers (which may be in one or more individual layers), preferably at least 40 wt.%, more
preferably at least 50 wt.%, even more preferably at least 60 wt.%, even more preferably at least 80 wt.%, even more preferably at least 90 wt.%, even more preferably at least 95 wt.%. In another embodiment, the stack comprises at least 5 wt.% of aramid-rich layers, in particular at least 10 wt.%, more in particular at least 15 wt.%, and even more in particular 20 wt.% of aramid-rich layers.

For polyethylene, the linear tension members preferably are polyethylene tapes. For preferred width and thickness specification of the tapes, reference is made to what is stated above for tapes in general. It is essential that the tapes be suitable for use in ballistic applications, which, more specifically, requires that they have a high tensile strength, a high tensile modulus and a high energy absorption, reflected in a high energy-to-break. It is preferred for the tapes to have a tensile strength of at least 1.0 GPa, a tensile modulus of at least 40 GPa, and a tensile energy-to-break of at least 15 J/g.

In one embodiment, the tensile strength of the tapes is at least 1.2 GPa, more in particular at least 1.5 GPa, still more in particular at least 1.8 GPa, even more in particular at least 2.0 GPa. In a particularly preferred embodiment, the tensile strength is at least 2.5 GPa, more in particular at least 3.0 GPa, still more in particular at least 4 GPa.

In another embodiment, the tapes have a tensile modulus of at least 50 GPa. The modulus is determined in accordance with ASTM D882-00. More in particular, the tapes may have a tensile modulus of at least 80 GPa, more in particular at least 100 GPa. In a preferred embodiment, the tapes have a tensile modulus of at least 120 GPa, even more in particular at least 140 GPa, or at least 150 GPa. The modulus is determined in accordance with ASTM D882-00.
In another embodiment, the tapes have a tensile energy to break of at least 20 J/g, in particular at least 25 J/g. In a preferred embodiment the polyethylene tapes have a tensile energy to break of at least 30 J/g, in particular at least 35 J/g, more in particular at least 40 J/g, still more in particular at least 50 J/g. The tensile energy to break is determined in accordance with ASTM D882-00 using a strain rate of 50%/min. It is calculated by integrating the energy per unit mass under the stress-strain curve.

More details on suitable types of polyethylene tapes and fibers and methods for the manufacture thereof will be provided below.

The aramid linear tension members may be fibers or tapes. The fibers may be monofilament yarn or multifilament yarn. Suitable aramid fibers consist of aramid filaments having a tenacity of at least 2.6 GPa, more preferably of at least 3.1 GPa and most preferably of at least 3.6 GPa, and a modulus of at least 60 GPa, more preferably of at least 75 GPa and most preferably of at least 90 GPa. Dependent on the amount of filaments and the type of twist applied the properties of the thus obtained twisted fibers or yarns vary. Under normal circumstances the twisted yarns have a tenacity of at least 2.1 GPa, more preferably of at least 2.6 GPa, even more preferably of at least 3.1 and most preferably of at least 3.6 GPa, and a modulus of at least 60 GPa, more preferably of at least 80 GPa and most preferably of at least 100 GPa.

In one embodiment, aramid tapes are used. In one embodiment, the aramid tapes are obtained by parallel aligning of aramid fibers and causing them to adhere via a matrix material. Optionally, they can be caused to adhere by the alternative or additional provision of weft yarns to keep the fibers.

Specific embodiments

5

The ballistic material of the present invention comprises a stack of sheets comprising reinforcing linear tension members. In the following, a number of specific embodiments of the present invention will be discussed.

In one embodiment, the stack is a compressed stack, in which the individual sheets are adhered to each other to provide a ballistic panel, for example, for use in ballistic vests. In another embodiment the stack comprises substacks of for example 2-10 sheets. Said substacks may be compressed substacks and/or flexible substacks. A flexible substack may be obtained, for example, by stitching the edges of the sheets together. A compressed substack may be a consolidated package of a number of sheets, for example, from 2 to 8 sheets, e.g., as a rule 2, 4 or 8 sheets. Consolidated is intended to mean that the sheets are firmly attached to one another. The sheets may be consolidated by the application of heat and/or pressure, as is known in the art.

In another embodiment, the stack comprises substacks of, for example 2-10 sheets, which substacks are combined at the edges to form a flexible ballistic stack.

In one embodiment, the stack comprises at least two substacks, wherein a first substack is a consolidated stack and a second substack is a flexible substack present below (from the strike-side of the panel) the first substack. In this embodiment the first substack is preferably a polyethylene-rich layer, and the second substack preferably is an aramid-rich layer.
In one embodiment the stack comprises a compressed substack of sheets comprising polyethylene and/or aramid linear tension members and a flexible substack comprising polyethylene and/or aramid linear tension members. The flexible substack may be for example stitched onto the compressed substack or adhered onto the compressed substack or the substacks may be held together on the edges or by placing them in a bag or a cover.

With respect to the total amount of linear tension members in the stack, in one embodiment, the stack comprises 1-20 wt.% of aramid linear tension members, in particular 1-10 wt.%, and, preferably, 80-99 wt.% of polyethylene linear tension members, in particular 90-99 wt.% (all percentages calculated on the total weight of linear tension members).

In another embodiment, the stack comprises 15-40 wt.% of aramid linear tension members, in particular 15-30 wt.%, and, preferably, 85-60 wt.% of polyethylene linear tension members, in particular 85-70 wt.% (all percentages calculated on the total weight of linear tension members).

In one embodiment of the present invention the ballistic resistant article is a stack, in particular a moulded stack, which comprises from top (i.e. strike face) to bottom a first layer and a second layer, wherein the first layer comprises sheets based on polyethylene linear tension members, in particular polyethylene tapes. In this embodiment, the linear tension members in the first layer consist for at least 70 wt.% of polyethylene, in particular for at least 80wt.%, still more in particular for at least 90 wt.%, yet more in particular for at least 95 wt.%.

In one embodiment the linear tension members in the first layer consist essentially of polyethylene. For the nature of the polyethylene reference is made to the preferences expressed elsewhere in this document. Where polyethylene tapes are used, it is preferred for the
first layer to contain 0-12 wt.% of a matrix material. While some matrix material may be required to cause the tapes to adhere together, the provision of more than 12 wt.% of matrix material may not be required, and may be detrimental to the ballistic properties of the panel.

The first layer of the stack preferably makes up between 20 and 99 wt.% of the stack. In one embodiment, the first layer makes up between 30 and 90 wt.% of the stack, in particular between 30 and 80 wt.%, more in particular between 30 and 70 wt.% of the stack, more in particular between 40 and 60 wt.%. In another embodiment, the first layer makes up between 50 and 99 wt.% of the stack, in particular between 60 and 99 wt.%, more in particular between 70 and 99 wt.%. In a further embodiment, the first layer may make up between 80 and 99 wt.%, more in particular between 90 and 99 wt.%, or even between 95 and 99 wt.%

The second layer of the ballistic material of this embodiment comprises sheets which contain aramid linear tension members, in particular aramid fibers. In this embodiment, the linear tension members in the second layer consist for at least 70 wt.% of aramid material, in particular for at least 80 wt.%, still more in particular for at least 90 wt.%. In one embodiment the linear tension members in the second layer consist essentially of aramid material. The aramid linear tension members are preferably fibers.

In the aramid-rich layer a matrix material may also be present. In the case of fibers, this may, for example, be in the range of 5-30 wt.%, more in particular in the range of 15 wt.%.

The ballistic panel of this embodiment may, for example, meet the requirements of class II of the NIJ Standard - 0101.04 P-BFS performance test. In a preferred embodiment, the requirements of class Ilia of said Standard are met, in an
even more preferred embodiment, the requirements of class III are met, or the requirements of even higher classes. This ballistic performance is preferably accompanied by a low areal weight, in particular an areal weight of at most 19 kg/m², more in particular at most 16 kg/m². In some embodiments, the areal weight of the stack may be as low as 15 kg/m². The minimum areal weight of the stack is given by the minimum ballistic resistance required.

In a particular embodiment the stack is a compressed stack of sheets or of consolidated sheet packages wherein the first layer consists essentially of polyethylene linear tension members and the second layer consists essentially of aramid linear tension members. The stack may comprise at least 80 wt.% of polyethylene, more in particular at least 90 wt.% of polyethylene, even more in particular at least 95 wt.% of polyethylene.

In another a particular embodiment the first polyethylene-rich layer is a compressed substack and the second aramid-rich layer is a flexible substack. The stack may comprise at least 80 wt.% of polyethylene, more in particular at least 90 wt.% of polyethylene, even more in particular at least 95 wt.% of polyethylene. The compressed substack of this embodiment may comprise sheets consisting essentially of polyethylene linear tension members and optionally may further comprise sheets consisting essentially of aramid linear tension members. For example the compressed substack may consist essentially of polyethylene or may generally comprise at least 1 wt.% of aramid, in particular at least 5 wt.% of aramid, more in particular at least 10 wt.% of aramid or even more in particular 20 wt.% of aramid. The flexible substack of this embodiment may comprise sheets consisting essentially of aramid linear tension members and
optionally may further comprises sheets consisting essentially of polyethylene linear tension members. The flexible substack preferably consists essentially of aramid linear tension members.

In another embodiment of the present invention the ballistic resistant article is a stack, in particular a moulded stack, which comprises from top to bottom a first layer and a second layer, wherein each layer is a compressed substack. In a particular embodiment both layers are polyethylene-rich layers and the composition of each polyethylene-rich layer may be the same or different. In a yet more particular embodiment the compressed substack at or closer to the strike face comprises sheets consisting essentially of polyethylene linear tension members and sheets consisting essentially of aramid linear tension members compressed together, whereas the second layer comprises sheets consisting essentially of polyethylene linear tension members.

In a further embodiment the ballistic resistant article is a stack comprising from top to bottom, a compressed layer and a flexible layer, wherein the compressed layer comprises from top to bottom a first polyethylene-rich layer and a second aramid-rich layer, and wherein the flexible layer is an aramid-rich layer. The total stack preferably comprises 60-99 wt.% of polyethylene, preferably 75-90 wt.% of polyethylene, and 40-1 wt.% of aramid, preferably 25-10 wt.% of aramid. The aramid-rich layer preferably makes up 1-15, preferably 1-10 wt.% of the compressed stack.

In another embodiment of the present invention a curved ballistic item, in particular a helmet, is envisaged which comprises, from top to bottom, an aramid-rich layer, preferably an all-aramid layer, a polyethylene-rich layer,
preferably an all-polyethylene layer, and a further aramid-rich layer.

For all embodiments: The polyethylene linear tension members are preferably tapes as discussed above. The aramid linear tension members are preferably fibers as discussed above.

The matrix material

As indicated above, a matrix material may be present in the ballistic material according to the invention. This is of particular interest where the ballistic-resistant article is a moulded article, as in that case a matrix material may be used to cause the individual sheets to adhere to each other.

The term "matrix material" means a material which binds the linear tension members and/or the sheets together. Where the linear tension members are fibers, matrix material may be required to adhere the fibres together to form unidirectional sheets. The use of sheets comprising woven linear tension members dispenses with the necessity of using matrix material for this reason, as the members are bonded together through their woven structure. Therefore, this will allow the use of less matrix material or even dispense with the use of matrix material altogether.

In one embodiment of the present invention the ballistic-resistant moulded article does not contain a matrix material. While it is believed that the matrix material has a lower contribution to the ballistic effectivity of the system than the tapes, the matrix-free embodiment may make an efficient material as regards its ballistic effectivity per weight ratio.

In another embodiment of the present invention, the ballistic resistant article comprises a matrix material. In this
embodiment, the matrix material may be present to improve the delamination properties of the material. It may also contribute to the ballistic performance.

5 In one embodiment of the present invention, matrix material is provided within the sheets themselves, where may help to adhere the linear tension members to each other, for example to provide a sheet of unidirectional fibers, or to stabilise a fabric after weaving.

10 In another embodiment of the present invention, matrix material is provided on the sheet, to adhere the sheet to further sheets within the stack.

One way of providing the matrix material onto the sheets is the provision of one or more films of matrix material on the top side, bottom side or both sides of the sheets. If so desired, the films may be caused to adhere to the sheet, e.g., by passing the films together with the sheet through a heated pressure roll or press.

Another way of providing the matrix material onto the sheets is by applying an amount of a liquid substance containing the organic matrix material onto the sheet. This embodiment has the advantage that it allows simple application of matrix material. The liquid substance may be for example a solution, a dispersion, or a melt of the organic matrix material. If a solution or a dispersion of the matrix material is used, the process also comprises evaporating the solvent or dispersant.

Further-more, the matrix material may be applied in vacuo. The liquid material may be applied homogeneously over the entire surface of the sheet, as the case may be. However, it is also possible to apply the matrix material in the form of a liquid material inhomogeneously over the surface of the sheet, as the case may be. For example, the liquid material may be applied in the form of dots or stripes, or in any other suitable pattern.
In one embodiment of the present invention the matrix material is applied in the form of a web, wherein a web is a discontinuous polymer film, that is, a polymer film with holes. This allows the provision of low weights of matrix materials.

In another embodiment of the present invention, the matrix material is applied in the form of strips, yarns, or fibres of polymer material, the latter for example in the form of a woven or non-woven yarn of fibre web or other polymeric fibrous weft. Again, this allows the provision of low weights of matrix materials.

In various embodiments described above, the matrix material is distributed inhomogeneously over the sheets. In one embodiment of the present invention the matrix material is distributed inhomogeneously within the compressed stack. In this embodiment more matrix material may be provided there were the compressed stack encounters the most influences from outside which may detrimentally affect stack properties.

The matrix material may wholly or partially consist of a polymer material, which optionally may contain fillers usually employed for polymers. The polymer may be a thermoset or thermoplastic or mixtures of both. Preferably a soft plastic is used, in particular it is preferred for the organic matrix material to be an elastomer with a tensile modulus (at 25°C) of at most 41 MPa. The use of non-polymeric organic matrix material is also envisaged. The purpose of the matrix material is to help to adhere the tapes and/or the sheets together where required, and any matrix material which attains this purpose is suitable as matrix material. Preferably, the elongation to break of the organic matrix material is greater than the elongation to break of the reinforcing tapes. The elongation to break of the matrix preferably is from 3 to
500%. These values apply to the matrix material as it is in the final ballistic-resistant article.

Thermosets and thermoplastics that are suitable for the sheet are listed in for instance EP 833742 and WO-A-91/12136. Preferably, vinylesters, unsaturated polyesters, epoxides or phenol resins are chosen as matrix material from the group of thermosetting polymers. These thermosets usually are in the sheet in partially set condition (the so-called B stage) before the stack of sheets is cured during compression of the ballistic-resistant moulded article. From the group of thermoplastic polymers polyurethanes, polyvinyls, polyacrylates, polyolefins or thermoplastic, elastomeric block copolymers such as polyiso-prene-polyethylene-butylene-polystyrene or polystyrene-polyisoprene-polystyrene block copolymers are preferably chosen as matrix material.

When a matrix material is used, it generally applied in an amount of at least 0.2 wt.%. It may be preferred for the matrix material to be present in an amount of at least 1 wt.%, more in particular in an amount of at least 2 wt.%, in some in-stances at least 2.5 wt.%. Matrix material is generally applied in an amount of at most 30 wt.%. The use of more than 30 wt.% of matrix material generally does not improve the properties of the moulded article.

The amount of matrix material will also depend on whether the linear tension members are tapes or fibers. In the case of fibers, a matrix material may be used to provide a sheet containing parallel fibers adhered together. In this case, a matrix content of the sheet of 10-30 wt.% may be mentioned, in particular 15-25 wt.%.

Where the linear tension members are tapes, it may be preferred to use a lower amount of matrix material. In some embodiments it may be preferred for the matrix material to be
within an amount of at most 12 wt.%, preferably at most 8 wt.%, more preferably at most 7 wt.%, sometimes at most 6.5 wt.%.

Aramid, chemical composition

Within the context of the present specification the word aramid refers to linear macromolecules made up of aromatic groups, wherein at least 60% of the aromatic groups are joined by amide, imide, imidazole, oxazolone or thiazole linkages and at least 85% of the amide, imide, imidazole, oxazolone or thiazole linkages are joined directly to two aromatic rings with the number of imide, imidazole, oxazolone or thiazole linkages not exceeding the number of amide linkages.

In a preferred embodiment, at least 80% of the aromatic groups are joined by amide linkages, more preferably at least 90%, still more preferably at least 95%.

In one embodiment, of the amide linkages, at least 40% are present at the para-position of the aromatic ring, preferably at least 60%, more preferably at least 80%, still more preferably at least 90%. Preferably, the aramid is a para-aramid, that is, an aramid wherein essentially all amide linkages are adhered to the para-position of the aromatic ring.

In one embodiment of the present invention the aramid is an aromatic polyamide consisting essentially of 100 mole% of:

A. at least 5 mole% but less than 35 mole%, based on the entire units of the polyamide, of units of formula (1)
wherein Ar\textsuperscript{1} is a divalent aromatic ring whose chain-extending bonds are coaxial or parallel and is a phenylene, biphenylene, naphthylene or pyridylene, each of which may have a substituent which is a lower alkyl, lower alkoxy, halogen, nitro, or cyano group, X is a member selected from the group consisting of O, S and NH, and the NH group bonded to the benzene ring of the above benzoxazole, benzothiazole or benzimidazole ring is meta or para to the carbon atom to which X is bonded of said benzene ring;

b. 0 to 45 mole\%, based on the entire units of the polyamide, of units of formula (2)

\begin{equation}
\text{-NH-\textsuperscript{Ar\textsuperscript{2}}-NH-}
\end{equation}

wherein Ar\textsuperscript{2} is the same in definition as Ar\textsuperscript{1}, and is identical to or different from Ar\textsuperscript{1}, or is a compound of formula (3)

\begin{equation}
\text{-C-O-\textsuperscript{Ar\textsuperscript{3}}-C-O-}
\end{equation}

c. an equimolar amount, based on the total moles of the units of formulae (1) and (2) above, of a structural unit of formula (4)
wherein $\text{Ar}^3$ is

![Chemical structures](attachment:chemical_structures.png)

in which the ring structure optionally contains a substituent selected from the group consisting of halogen, lower alkyl, lower alkoxy, nitro and cyano; and

D. 0 to 90 mole%, based on the entire units of the polyamide, of a structural unit of formula (5) below

\[-\text{NH} - \text{Ar}^4 - \text{CO} -\]

wherein $\text{Ar}^4$ is the same in definition as $\text{Ar}^1$, and is identical to or different from $\text{Ar}^1$.

The preferred aramid is poly (p-phenylene terephthalamide) which is known as PPTA. PPTA is the homopolymer resulting from mole-for-mole polymerization of p-phenylenediamine and terephthaloyl chloride. Another preferred aramid are co-polymers resulting from incorporation of other diamines or diacid chlorides replacing p-phenylenediamine and terephthaloyl chloride respectively.

**Polyethylene, chemical composition and manufacture**

The polyethylene used in the present invention, whether indicated as polyethylene, high-molecular weight polyethylene, or ultra-high molecular weight polyethylene, has a a weight average molecular weight of at least 300 000 g/mol. Linear polyethylene here means polyethylene having fewer than 1 side chain per 100 C atoms, preferably fewer than 1 side chain per 300 C atoms. The polyethylene may also contain up to 5 mol %
of one or more other alkenes which are copolymerisable therewith, such as propylene, butene, pentene, 4-methylpentene, and octene. It may be particularly preferred for the polyethylene to have a weight average molecular weight of at least 500,000 g/mol. The use of tapes, in particular fibres or tapes, with a molecular weight of at least $1 \times 10^8$ g/mol may be particularly preferred. The maximum molecular weight of the polyethylene suitable for use in the present invention is not critical. As a general value a maximum value of $1 \times 10^8$ g/mol may be mentioned. The molecular weight distribution may be determined as is described in WO2009/109632.

In one embodiment of the present invention, polyethylene linear tension members are used with a relatively narrow molecular weight distribution. This is expressed by the $M_w$ (weight average molecular weight) over $M_n$ (number average molecular weight) ratio of at most 6. More in particular the $M_w/M_n$ ratio is at most 5, still more in particular at most 4, even more in particular at most 3. The use of materials with an $M_w/M_n$ ratio of at most 2.5, or even at most 2 is envisaged in particular.

In a preferred embodiment of the present invention the polyethylene tapes with a high molecular weight and the stipulated narrow molecular weight distribution have a high molecular orientation as is evidenced by their XRD diffraction pattern.

In one embodiment of the present invention, the polyethylene linear tension members are tapes having a 200/110 uniplanar orientation parameter $\Phi$ of at least 3. The 200/110 uniplanar orientation parameter $\Phi$ is defined as the ratio between the 200 and the 110 peak areas in the X-ray diffraction (XRD) pattern of the tape sample as determined in reflection geometry. Wide angle X-ray scattering (WAXS) is a technique that provides information on the crystalline structure of
matter. The technique specifically refers to the analysis of Bragg peaks scattered at wide angles. Bragg peaks result from long-range structural order. A WAXS measurement produces a diffraction pattern, i.e. intensity as function of the diffraction angle $2\Theta$ (this is the angle between the diffracted beam and the primary beam). The 200/110 uniplanar orientation parameter gives information about the extent of orientation of the 200 and 110 crystal planes with respect to the tape surface. For a tape sample with a high 200/110 uniplanar orientation the 200 crystal planes are highly oriented parallel to the tape surface. It has been found that a high uniplanar orientation is generally accompanied by a high tensile strength and high tensile energy to break. The ratio between the 200 and 110 peak areas for a specimen with randomly oriented crystallites is around 0.4. However, in the tapes that are preferentially used in one embodiment of the present invention the crystallites with indices 200 are preferentially oriented parallel to the film surface, resulting in a higher value of the 200/110 peak area ratio and therefore in a higher value of the uniplanar orientation parameter. The UHMWPE tapes with narrow molecular weight distribution used in one embodiment of the ballistic material according to the invention have a 200/110 uniplanar orientation parameter of at least 3. It may be preferred for this value to be at least 4, more in particular at least 5, or at least 7. Higher values, such as values of at least 10 or even at least 15 may be particularly preferred. The theoretical maximum value for this parameter is infinite if the peak area 110 equals zero. High values for the 200/110 uniplanar orientation parameter are often accompanied by high values for the strength and the energy to break. For a determination method of this parameter reference is made to WO2009/109632.
In one embodiment of the present invention, the UHMWPE tapes, in particular UHMWPE tapes with an Mw/MN ratio of at most 6 have a DSC crystallinity of at least 74%, more in particular at least 80%. The DSC crystallinity can be determined as follows using differential scanning calorimetry (DSC), for example on a Perkin Elmer DSC7. Thus, a sample of known weight (2 mg) is heated from 30 to 180°C at 10°C per minute, held at 180°C for 5 minutes, then cooled at 10°C per minute. The results of the DSC scan may be plotted as a graph of heat flow (mW or mJ/s; y-axis) against temperature (x-axis). The crystallinity is measured using the data from the heating portion of the scan. An enthalpy of fusion $\Delta H$ (in J/g) for the crystalline melt transition is calculated by determining the area under the graph from the temperature determined just below the start of the main melt transition (endotherm) to the temperature just above the point where fusion is observed to be completed. The calculated $\Delta H$ is then compared to the theoretical enthalpy of fusion ($\Delta H_f$ of 293 J/g) determined for 100% crystalline PE at a melt temperature of approximately 140°C. A DSC crystallinity index is expressed as the percentage 100 ($\Delta H/\Delta H_f$). In one embodiment, the tapes used in the present invention have a DSC crystallinity of at least 85%, more in particular at least 90%.

In general, the polyethylene linear tension members, have a polymer solvent content of less than 0.05 wt.%, in particular less than 0.025 wt.%, more in particular less than 0.01 wt.%. In one embodiment the polyethylene tapes used in the present invention may have a high strength in combination with a high linear density. In the present application the linear density is expressed in dtex. This is the weight in grams of 10.000 metres of film. In one embodiment, the film according to the invention has a linear density of at least 3000 dtex, in particular at least 5000 dtex, more in particular at least 10000 dtex, even more in particular at least 15000 dtex, or
even at least 20000 dtex, in combination with strengths of, as specified above, at least 2.0 GPa, in particular at least 2.5 GPA, more in particular at least 3.0 GPa, still more in particular at least 3.5 GPa, and even more in particular at least 4.

Suitable tapes for use in the present invention encompass those described in WO2009/109632, the relevant parts of which are incorporated herein by reference.

In one embodiment, the present invention pertains to the manufacture of ballistic articles according to the present invention by a process comprising the steps of providing sheets comprising linear tension members, stacking the sheets in such a manner that the direction of the linear tension members within the stack is not unidirectionally, and adhering at least some of the sheets to each other wherein some of the linear tension members are linear tension members comprising ultra-high molecular weight polyethylene and some of the linear tension members comprise aramid. The adhering of the sheets can be done in manners known in the art. In the manufacture of soft-ballistics this can, e.g., be done by stitching the edges of the sheets together to form sheet packages. In one embodiment, moulded ballistic panels are manufactured by a process comprising the steps of providing sheets comprising linear tension members, stacking the sheets in such a manner that the direction of the linear tension members within the stack is not unidirectionally, and compressing the stack under a pressure of at least 0.5 MPa. The pressure to be applied is intended to ensure the formation of a ballistic-resistant moulded article with adequate properties. The pressure is at least 0.5 MPa. A maximum pressure of at most 50 MPa may be mentioned. Where necessary, the temperature during compression is selected such that the matrix material is brought above its softening or melting.
point, if this is necessary to cause the matrix to help adhere the linear tension members and/or sheets to each other. Compression at an elevated temperature is intended to mean that the moulded article is subjected to the given pressure for a particular compression time at a compression temperature above the softening or melting point of the organic matrix material and below the softening or melting point of the linear tension members. The required compression time and compression temperature depend on the nature of the linear tension members and matrix material and on the thickness of the moulded article and can be readily determined by the person skilled in the art. Where the compression is carried out at elevated temperature, it may be preferred for the cooling of the compressed material to also take place under pressure. Cooling under pressure is intended to mean that the given minimum pressure is maintained during cooling at least until so low a temperature is reached that the structure of the moulded article can no longer relax under atmospheric pressure. It is within the scope of the skilled person to determine this temperature on a case by case basis. Where applicable it is preferred for cooling at the given minimum pressure to be down to a temperature at which the organic matrix material has largely or completely hardened or crystallized and below the relaxation temperature of the linear tension members. The pressure during the cooling does not need to be equal to the pressure at the high temperature. During cooling, the pressure should be monitored so that appropriate pressure values are maintained, to compensate for decrease in pressure caused by shrinking of the moulded article and the press.

Depending on the nature of the matrix material, for the manufacture of a ballistic-resistant moulded article in which the linear tension members in the sheet comprise high-drawn tapes of high-molecular weight linear polyethylene, the
compression temperature is preferably 115 to 135°C and cooling to below 70°C is effected at a constant pressure. Within the present specification the temperature of the material, e.g., compression temperature refers to the temperature at half the thickness of the moulded article.

In one embodiment of the present invention, the stack is built up from consolidated sheet packages containing from 2 to 8, as a rule 2, 4 or 8. For the orientation of the sheets within the sheet packages, reference is made to what has been stated above for the orientation of the sheets within the stack. Consolidated is intended to mean that the sheets are firmly attached to one another. Very good results are achieved if the sheet packages, too, are compressed. The sheets may be consolidated by the application of heat and/or pressure, as is known in the art.

Examples

Several ballistic materials were manufactured as follows. Compressed stacks or substacks were manufactured by cross-plying sheets of the appropriate materials and amounts to form a stack. The stack was compressed at a temperature of 132 °C, at a pressure of 60 bar. The material was cooled down and removed from the press to form a compressed stack or substack.

Flexible substacks were manufactured by stitching the edges of individual sheets together.

If the substacks were not moulded simultaneously to form a single stack the substacks were held together before shooting.

The panels had a total areal weight of 15.5 kg/m2.
PE sheets were manufactured by aligning tapes in parallel to form a first layer, aligning at least one further layer of tapes onto the first layer parallel and offset to the tapes in the first layer, and heat-pressing the tape layers to form a sheet. UHMW polyethylene tapes with a width of 80 mm and a thickness of 55 µm were used. The tapes had a tensile strength of 2.3 GPa, a tensile modulus of 165 GPa. A single type of PE sheets was used. The sheets of type A are 0-90° X-plies of approximately 220 µm thickness (matrix content: 3 wt.%)

Two types of aramid sheets were used. Laminated aramid sheets were manufactured by unidirectionally aligning PPTA aramid fibers in a styrene-isoprene-styrene matrix with an outer coating of low-molecular weight PE (matrix content about 20 wt.%). This system will be indicated as aramid UD. Sheets based on aramid fabric were made by an aramid fabric, commercially known as Twaron CT 736 fabric from Teijin, with polyphenolic resin as matrix (matrix content 11 wt.%). This system will be indicated as aramid textile.

Different panels were manufactured with varying amounts of PE and aramid according to Table 1, by appropriately stacking the corresponding PE-based sheets and/or aramid-based sheets.

The PE:aramid ratios correspond to wt.% of polyethylene sheets (including matrix) with respect to wt.% of aramid sheets (including matrix) based on the total weight of the system.

Table 1: Composition of the panels

<table>
<thead>
<tr>
<th>Panel</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comp. 1</td>
<td>100% PE, compressed</td>
</tr>
<tr>
<td>Comp. 2</td>
<td>100% PE, compressed</td>
</tr>
<tr>
<td>Comp. 3</td>
<td>100% PE, compressed</td>
</tr>
<tr>
<td>Ex. 1</td>
<td>80% PE layer, 20% aramid UD layer, compressed in single stack</td>
</tr>
<tr>
<td>Ex. 2</td>
<td>1st substack: compressed stack of 80% PE and 3% aramid textile sheet</td>
</tr>
<tr>
<td>Ex. 3</td>
<td>2nd substack: flexible stack of 17% aramid UD</td>
</tr>
<tr>
<td>Ex. 1</td>
<td>97% PE layer, 3% aramid textile layer, compressed in single stack</td>
</tr>
</tbody>
</table>
The panels were tested for trauma evaluation in accordance with NIJ III 01.04.04. The velocity used ranged from 838 to 856 m/s. It was found that the bullets were stopped in the panel. The results of the comparative panels, which all have the same composition, are averaged.

Table 2: Performance of the panels

<table>
<thead>
<tr>
<th>Panel</th>
<th>Bullet stop</th>
<th>Trauma [mm]</th>
<th>Relative trauma</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comp.</td>
<td>SIP</td>
<td>44</td>
<td>-</td>
</tr>
<tr>
<td>Ex.1</td>
<td>SIP</td>
<td>44</td>
<td>1%</td>
</tr>
<tr>
<td>Ex.2</td>
<td>SIP</td>
<td>42</td>
<td>-5%</td>
</tr>
<tr>
<td>Ex.3</td>
<td>SIP</td>
<td>44</td>
<td>1%</td>
</tr>
<tr>
<td>Ex.4</td>
<td>SIP</td>
<td>42</td>
<td>-4%</td>
</tr>
</tbody>
</table>

1. SIP: Bullet stopped in panel
2. Average value from 3 different shoots
3. Relative trauma refers to the percentage of increase or decrease of trauma, with positive and negative percentages respectively, of the hybrid panels (PE plus aramid) with respect to the panels comprising PE only with the same type of PE.
4. Average reference value from 9 different shoots on three different panels

The results of Table 2 show that the performance of the hybrid panels, i.e. comprising both polyethylene and aramid (Examples 1-5) is equivalent to that of panels consisting of polyethylene or is even improved with respect to the reduction of trauma (Examples 2 and 4). It is noted that the generally accepted maximum amount of trauma is 44 mm.

Figures 1 through 3 are pictures of the front and the back of the panels of Comparative Example 1 and Examples 1 and 3, taken after 5 shots.

As can be seen from the pictures the back of the ballistic panels is notably improved in the materials comprising aramid
(Examples 1 and 3), whereby the bullet fragments stay within the antiballistic panel and the back of the panel is improved with respect to that of all polyethylene (Comparative Example 1).
CLAIMS

1. Ballistic-resistant article comprising a stack of sheets comprising reinforcing linear tension members, the direction of the linear tension members within the stack being not unidirectionally, wherein some of the linear tension members are linear tension members comprising high molecular weight polyethylene and some of the linear tension members comprise aramid.

2. Ballistic-resistant article according to claim 1, wherein the linear tension members comprising high molecular weight polyethylene are polyethylene tapes with a width of at least 5 mm.

3. Ballistic-resistant article according claim 1 or 2, wherein the linear tension members comprising aramid are PPTA fibers.

4. Ballistic-resistant article according to any one of the preceding claims wherein the stack comprises sheets which contain both polyethylene linear tension members and aramid linear tension members.

5. Ballistic-resistant article according to any one of the preceding claims wherein the stack comprises sheets which comprise polyethylene linear tension members and are free of aramid-type linear tension members and/or sheets which comprise aramid-type linear tension members and are free of polyethylene linear tension members.

6. Ballistic-resistant article according to any one of the preceding claims wherein linear tension members in the sheets are unidirectionally oriented, and the direction of the linear
tension members in a sheet is rotated with respect to the
direction of the tapes in an adjacent sheet.

7. Ballistic-resistant article according to any one of claims
   1-5 wherein a sheet comprises woven linear tension members.

8. Ballistic-resistant article according to claim 7, wherein
   the sheet comprises one of polyethylene and aramid linear
tension members as warp or weft and the other of polyethylene
   and aramid linear tension members as weft or warp.

9. Ballistic-resistant article according to any one of the
   preceding claims wherein the polyethylene linear tension
   members and aramid linear tension members are distributed
   inhomogeneously over the thickness of the panel.

10. Ballistic-resistant article according to claim 9, wherein
    the stack comprises a layer which comprises more than 50 wt.%
    of polyethylene linear tension members and a layer which
    comprises more than 50 wt.% of aramid linear tension members.

11. Sheet comprising linear tension members, wherein some of
    the linear tension members comprise high molecular weight
    polyethylene, and some of the linear tension members comprise
    aramid.

12. Sheet according to claim 11, wherein the sheet is a woven
    sheet which comprises one of polyethylene and aramid-type
    linear tension members as warp or weft and the other of
    polyethylene and aramid-type linear tension members as weft or
    warp.

13. Consolidated sheet package suitable for use in the
    manufacture of a ballistic-resistant moulded article of any
one of the claims 1-10, wherein the consolidated sheet package comprises sheets comprising linear tension members the direction of the linear tension members within the sheet package being not unidirectionally, wherein some of the linear tension members are linear tension members comprising ultra-high molecular weight polyethylene, and some of the linear tension members comprise aramid.

14. Method for manufacturing a ballistic-resistant article according to any one of claims 1-10, comprising the steps of providing sheets comprising linear tension members, stacking the sheets in such a manner that the direction of the linear tension members within the stack is not unidirectionally, and adhering at least some of the sheets to each other wherein some of the linear tension members are linear tension members comprising ultra-high molecular weight polyethylene and some of the linear tension members comprise aramid.

15. Method according to claim 14, wherein a moulded article is manufactured by a process comprising the steps of providing sheets comprising linear tension members, stacking the sheets in such a manner that the direction of the linear tension members within the stack is not unidirectionally, and compressing the stack under a pressure of at least 0.5 MPa.
Figure 1: Front and back of Comparative Example 1 panel after 5 shots
Figure 2: Front and back of Example 1 panel after 5 shots
Figure 3: Front and back of Example 3 panel after 5 shots
# INTERNATIONAL SEARCH REPORT

## A. CLASSIFICATION OF SUBJECT MATTER

**INV. 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)

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, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>WO 2008/048301 A2 (HONEYWELL INT INC [US]); PALLEY IGOR [US]) 24 April 2008 (2008-04-24) page 2, line 9 - page 4, line 12; claims 1,19,24,35,40,41,43; figures 1,2</td>
<td>1-8, 10-15</td>
</tr>
<tr>
<td>Y</td>
<td>WO 2005/098343 A1 (TUNIS GEORGE [US]) 20 October 2005 (2005-10-20) page 7, line 3 - page 12, line 12; figures 4-10</td>
<td>9</td>
</tr>
</tbody>
</table>

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
  
  "E" earlier document but published on or after the international filing date
  
  "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
  
  "O" document referring to an oral disclosure, use, exhibition or other means
  
  "P" document published prior to the international filing date but later than the priority date claimed
  
  "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
  
  "X" document of particular relevance; the claimed invention cannot be considered to be obvious over such document
  
  "Y" document of particular relevance; the claimed invention cannot be considered to be obvious over such document
  
  "A" document member of the same patent family

Date of the actual completion of the international search:

19 April 2011

Date of mailing of the international search report:

29/04/2011

Name and mailing address of the ISA:

Beaufume, Cedric

European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-5040, Fax: (+31-70) 340-3016

Authorized officer

Form PCT/ISA/210 (second sheet) (April 2005)
<table>
<thead>
<tr>
<th>Patent document cited in search report</th>
<th>Publication date</th>
<th>Patent family member(s)</th>
<th>Publication date</th>
</tr>
</thead>
<tbody>
<tr>
<td>wo 2008048301 A2</td>
<td>24-04-2008</td>
<td>CN 101336163 A</td>
<td>31-12-2008</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EP 1960187 A2</td>
<td>27-08-2008</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP 2009518619 T</td>
<td>07-05-2009</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 2008119099 Al</td>
<td>22-05-2008</td>
</tr>
<tr>
<td>wo 2005098343 Al</td>
<td>20-10--2005</td>
<td>CA 2562349 Al</td>
<td>20-10-2005</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EP 1756509 Al</td>
<td>28-02-2007</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 2009169855 Al</td>
<td>02-07-2009</td>
</tr>
<tr>
<td>us 2008241494 Al</td>
<td>02-10--2008</td>
<td>CA 2681629 Al</td>
<td>09-10-2008</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CN 101680730 A</td>
<td>24-03-2010</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EP 2129992 A2</td>
<td>09-12-2009</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP 2010522657 T</td>
<td>08-07-2010</td>
</tr>
<tr>
<td></td>
<td></td>
<td>WO 2008121682 A2</td>
<td>09-10-2008</td>
</tr>
</tbody>
</table>