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(54) Title: IMPACT RESISTANT COMPOSITE MATERIAL

(57) Abstract: The invention relates to a preformed sheet with an improved ballistic resistance, comprising a network of fibers having a tensile strength of at least 1.5 GPa, impregnated with at least 10% of a plastic material comprising a multiphase (meth)acrylic based polymer dispersion. Such polymer dispersion has a first phase which has a minimum glass transition temperature of at least 40 °C and a weight average molecular weight of less than 80,000 g/mol and a second phase having a maximum glass transition temperature of 30 °C or less and a weight average molecular weight of more than 100,000 g/mol.

IMPACT RESISTANT COMPOSITE MATERIAL

The invention relates to a preformed sheet, comprising a network of fibers having a tensile strength of at least 1.5 GPa, which is impregnated with at least 10% of a plastic material. The invention further relates to an assembly of at least two preformed sheets and to a flexible ballistic-resistant article comprising said assembly.

US4623574 describes an improved, ballistic-resistant composite article, which comprises a network of fibers being a fabric or substantially parallel, unidirectionally aligned fibers and a matrix material with a tensile modulus at 23 ºC of less than 41,3 MPa and a glass transition temperature of less than 0 ºC, preferably less than -40 ºC. Disclosed matrix systems include Kraton® triblock polystyrene-polyisoprene-polystyrene copolymer.

WO2004039565A describes a process for the manufacture of a ballistic resistant article in which a stack of monolayers is formed, each monolayer containing unidirectionally oriented reinforcing fibers and at most 30 wt% of a plastic matrix material, the reinforcing fibers being highly-drawn polyethylene (UHMWPE), fibers and with the fiber direction in each monolayer being rotated with respect to the fiber direction in an adjacent monolayer. The plastic matrix material has a 100% modulus of between 5 and 500 MPa. It is shown that the claimed stiff plastic matrix matrix systems have high projectile stopping performance at higher temperature of 80 ˚C, whereas at room temperature softer matrix systems performs better.

EP0987363A1 describes the use of binder based on a cross-linkable unsaturated ethylene based polymer powder with a Tg of above 40 ˚C in the manufacture of ballistic resistant fabrics. There is no indication in EP0987363A1 of the presence of a multiphase (meth)acrylic based polymer dispersion. In Example 1 of this publication, 12 layers of aramid fabric are electrostatically spray coated with a powder comprising 98wt% of a styrene-butylacrylate copolymer with 5% acrylic acid and a Tg of 60 ˚C, and 5 wt% epoxy crosslinking agent, followed by curing for 2 minutes at 170 ˚C and stacking the layers with subsequent pressing for 1 minute at 1 bar at 180 ˚C to create a panel of 6mm thickness. In comparative experiment 3 an aqueous dispersion of a styrene-butylacrylate copolymer with 5% acrylic acid and 5 wt% epoxy crosslinking agent was coated on the aramid layers in a same amount of 30 grams as in example 1, followed by stacking 12 layers and 1 minute pressing at 1 bar at 180 °C to create a panel of a thickness of also 6mm thickness. Upon shooting from 10 m distance it proved that the panel of example 1 stopped all the bullets, while the panel of experiment 3 was completely penetrated by all bullets. Analysis of the panels with Scanning Electron Microscopy showed that the aramid fibers in example 1 were irregularly covered, while the fibers in example 3 were completely covered with the binder material.

Despite the fact that the known composite articles show reasonable antiballistic performance, there is a need for an increased bullet stopping power.

An objective of the present invention is to provide a flexible composite material that shows increased bullet stopping power than composites known so far.

This object is achieved by a plastic matrix material comprising an multiphase (meth)acrylic based polymer dispersion. Such polymer dispersion has a first phase which has a minimum glass transition temperature of at least 40 °C and a weight average molecular weight of less than 80,000 g/mol (oligomer phase) and a second phase having a maximum glass transition temperature of 30 °C or less and a weight average molecular weight of more than 100,000 g/mol (polymer phase)

An acrylic based system, comprising an oligomer and a polymer are well known in the art and mostly used as dispersion for the provision of films, paints, adhesives and coatings. When the oligomer is more hydrophilic than the polymer, the oligomer and the polymer tends to form a two-phase system, which in an extreme difference in hydrophilic properties of the two phases may result in a core-shell structure as e.g. described by Lee and Ishikawa (*The Formation of Inverted Core-Shell Latexes,* J. Poly. Sci., vol. 21, pages 147-154 (1983)).

Two-phase systems suitable for use in the current invention are furthermore known from WO95/29963, which is hereby incorporated by reference in its entirety. In these applications the low molecular weight component, referred to as oligomer or oligomer phase, is prepared first and the second high molecular weight component, referred to as polymer or polymer phase, is prepared in presence of the oligomer. It is also possible that the oligomer is blended with a polymer whereby the order of blending is not critical and may be chosen at will.

The oligomer is typically an acid functional oligomer comprising sufficient acid bearing comonomer(s) like acrylic acid, methacrylic acid, itaconic acid or beta-carboxy ethylacrylate to render the resulting oligomer fully or partly soluble in water. The acrylic oligomer may be based on acid group comprising precursors in an amount of 0.1-20 wt%, preferably 0.5-15wt%, more preferably 1.0.-12 wt%, and furthermore may be based on –OH functional monomers in an amount of between 0-30 wt%, preferably between 0-20 wt%, more preferably between 0-15 wt%, and most preferably between 0-10 wt%. The oligomer generally has an average weight molecular weight of between 500 and 80,000 g/mol, preferably 2,000 to 60,000, more preferably 5,000 to 50,000 and most preferably 10,000 to 40,000 g/mol. The Tg of the acrylic based oligomer is at least 25 °C, preferably at least 35 °C, more preferably at least 45 °C, even more preferably at least 55 °C. Usually, the Tg of oligomer will be within the range of from 25 to 120 °C, more usually from 30 to 90 °C.

The polymer, typically a hydrophobic polymer, comprises non-acid functional, non-crosslinking monomers and in particular methyl methacrylate, ethyl methacrylate, n-butyl methacrylate or t-butyl methacrylate. The weight average molecular weight of the acrylic polymer is usually at least 4,000 g/mol, more usually at least 80,000 g/mol. The upper limit usually does not exceed 3,000,000 g/mol. Typically the weight average molecular weight ranges between 40,000 g/mol and 3 000,000 g/mol, preferably between 80,000 g/mol and 2 000,000 g/mol, more preferably between 100,000 g/mol and 1000,000 g/mol. The glass transition temperature of the acrylic based thermoplastic polymer is at less than 30 °C, preferably less than 15 °C, more preferably less than 0 °C. Usually, the Tg of polymer will be within the range of from -60 to 30 °C, more usually from -30 to 10 °C.

The glass transition temperature of the oligomer is least 30 °C preferably 40 °C, more preferably 50 °C below the glass transition temperature of the polymer.

The preparation of the above-mentioned two phase systems bases on acrylic resins is e.g. described in WO 95/29944A1 and more preferably in WO95/29963. The two phase system may be cross linked. Methods for such are known to the skilled person.

In case of blending of an oligomer dispersion and a polymer dispersion the same Tg and weight average molecular weight ranges as described above apply. The weight ratio oligomer:polymer dispersion is between 10:90 to 70:30 (wt/wt), preferably 20:80 to 60:50 and most preferably 25:75 to 50:50.

The stopping power for bullets of armor is expressed as V_{50}, or relative to its weight/thickness as energy absorption, Eabs. The preformed sheet of the invention has an improved Eabs. The advantage of a high Eabs is that fragments or projectiles having a given velocity can be stopped by a layered article with a substantially lower areal mass. The areal mass indicates the mass per m^2 of surface of the article, and is also referred to as areal density. A low areal mass is very important for increasing the wearing comfort, which together with good protection is the main objective when developing new materials in ballistic-resistant clothing. A reduction in mass is also of advantage in case of e.g. vehicle or helicopter armouring.

Additional advantages of an article comprising a plurality of the preformed sheets according to the invention are an improved printability and stab resistance. Stab resistance in the art is known as being able to withstand stabbing with e.g. a knife. A product that is able to withstand both ballistic impact and stab is generally referred to as multi-threat use. At the same time the higher stiffness may result in end-products that have increased rigidity. Such is of importance for e.g. helmets (improved ‘ear-to-ear stiffness’), pressed inserts, especially when combined with ceramics, and structural vehicle parts. When used in soft body applications and the wearing comfort would need additional improvement, the preformed sheets of the invention may be (multiple) flexed, wrinkled or otherwise subjected to multiple bending to increase their flexibility.

The network of fibers may be a fabric (woven with e.g. plain, basket, satin and crow feet weaves), but it may also be a knitted network, or a network formed into a fabric in any of a variety of conventional techniques. For example, the fiber network could also be a "non-woven", including felt.

In the above-mentioned fiber networks, the acrylic based thermoplastic material is present in the preformed sheet in an amount of at most 70 wt%, preferably at most 60 wt% and more preferably at most 50 wt%. A network of fibers of the preformed sheet comprises at least 10%, preferably at least 20 wt% of the acrylic based thermoplastic material. Typically acrylic based thermoplastic material is present in the preformed sheet in an amount of between 10-60 wt%, preferably between 20-50 wt%, more preferably between 30-40 wt%.

A network of fibers may comprise a stack of two or more layers of fabric. In a stack of two or more fabric layers there may be an angle β between the two adjacent layers, wherein β is the smallest angle between two fiber directions in adjacent layers of the stack. The angle ß is typically in a range of between 0 and 45 degrees. Preferably the angle ß between two adjacent layers is 0 degrees.

Alternatively, the network of fibers comprises one or more monolayers of substantially parallel, unidirectionally aligned fibers.

Within the context of the present application monolayer means a layer of substantially parallel reinforcing fibers embedded in a plastic matrix material. The term matrix material means a material, which holds the fibers together and which preferably wholly or at least partially encapsulates the fibers. Such monolayers (also called prepregs by one skilled in the art) and the methods of obtaining such monolayers are disclosed in for instance EP 191306 and WO 95/00318 A1. A monolayer may be obtained by orienting a plurality of fibers in coplanar and parallel fashion in one plane, for instance by pulling a number of fibers or yarns from a fiber bobbin frame over a comb, and impregnating the fibers with the plastic matrix material in a known way before, during or after orienting. In this process, fibers may be used that have previously been coated with a polymer other than the plastic matrix material in order to, for instance, protect the fibers during handling or in order to obtain better adhesion of the fibers onto the plastic of the monolayer. Preferably, uncoated fibers are used. The fibers may have had a treatment before coating or contacting the fibers with the plastic matrix material. Such treatment included plasma or corona treatment.

In a preformed sheet with two or more layers, the direction of the aligned fibers in two subsequent monolayers in the stack typically differs by an angle α. Although the angle α may be selected within wide ranges, angle α is preferably between 45 and 135 degrees, more preferably between 65 and 115 degrees and most preferably between 80 and 100 degrees. In the latter preferred range a particularly preferred angle α is about 90 degrees. A preformed sheet produced according to this preferred embodiment is denoted as a cross ply in the art.

In a cross ply the fiber network occupies different proportions of the total volume of the sheet. Preferably, however, the fiber network comprises at least about 50 volume percent of the composite, more preferably between about 70 volume percent, and most preferably at least about 75 volume percent, with the matrix optionally occupying the remaining volume.

The term fiber comprises not only a monofilament but, inter alia, also a multifilament yarn or flat tapes. The term unidirectionally oriented fibers refers to fibers that, in one plane, are essentially oriented in parallel. Width of the flat tape preferably is between 2 mm and 100 mm, more preferably between 5 mm and 60 mm, most preferably between 10 mm and 40 mm. Thickness of the flat tape preferably is between 10 μm and 200 μm, more preferably between 25 μm and 100 μm. The flat tape may be composed of a single member of one material, but may also comprise unidirectionally oriented fibers and optionally a matrix material.

A preformed sheet of the present invention include a fiber network, which may include a polyolefin, an ultra-high molecular mass polyethylene fiber, an ultra-high molecular mass polypropylene fiber, an aramid fiber, an ultra-high molecular mass polyvinyl alcohol fiber, a fiber from a liquid crystalline polymer, or mixtures thereof. Suitable polyolefins are in particular homopolymers and copolymers of ethylene and propylene, which may also contain small quantities of one or more other polymers, in particular other alkene-1-polymers. Preferably the fiber network includes ultra-high molecular mass polyethylene fiber.

The fibers used in the network of the present invention have a strength of at least 1.5 GPa, preferably at least 2.5 GPa. More preferably the fibers used in the network of the present invention have a strength of at least at least 3.5 GPa which results in an even better combination of high projectile stopping performance and end products with increased rigidity and/or back face signature. Even more preferably the fibers used in the network of the present invention have a strength of at least 4GPa for obtaining products with better multi-threat performance, and most preferably at least 4.5 GPa.

Good results are obtained if linear polyethylene (PE) is selected as the polyolefin. Linear polyethylene is herein understood to mean polyethylene with less than 1 side chain per 100 C atoms, and preferably with less than 1 side chain per 300 C atoms; a side chain or branch generally containing at most 10 C atoms. The linear polyethylene may further contain up to 5 mol% of one or more other alkenes that are copolymerizable therewith, such as propene, butene, pentene, 4-methylpentene, octene. Preferably, the linear polyethylene is of high molar mass with an intrinsic viscosity (IV, as determined on solutions in decalin at 135°C) of at least 4 dl/g; more preferably of at least 8 dl/g. Such polyethylene is also referred to as ultra-high molecular mass polyethylene (UHPE).

High performance polyethylene (HPPE) fibers consisting of polyethylene filaments that have been prepared by a gel spinning process, such as described, for example, in GB 2042414 A or WO 01/73173, are preferably used. A gel spinning process essentially consists of preparing a solution of a linear polyethylene with a high intrinsic viscosity, spinning the solution into filaments at a temperature above the dissolving temperature, cooling down the filaments to below the gelling temperature, such that gelling occurs, and stretching the filaments before, during or after the removal of the solvent. This stretching results in drawn fibers that have a strength of at least 1.5 GPa. If these polyethylene fibers are highly drawn, they have a strength of at least 3.0 GPa.

The tapes as mentioned here above may also be made via a gel spinning process, but may also be obtained by a solid state process whereby polymer powder is compacted and drawn to obtain tapes with the desired strength.

The preformed sheet may, optionally, further comprise a separating film on, and bonded to, at least one of its outer surfaces. Such a separating film ensures that one or more preformed sheets in a ballistic resistant article or an assembly of preformed sheets of the invention, optionally combined with other sheets, remain separate from one another. This embodiment has the advantage that the flexibility, or wearing comfort of a ballistic resistant article or an assembly is higher. Such separating film in particular is preferable if a tacky matrix material is used. The separating film used may, for example, comprise a polyolefin film, including linear low-density polyethylene available under the Stamylex® trademark, polypropylene films, polyester films. Thickness of such films generally is between 1 and 50 micrometers, preferably between 2 and 25 micrometer. More preferably between 2 and 10 micrometer, and most preferably 3 and 6 micrometer

Preferably the separating film is a biaxially stretched polyolefin film. Examples hereof are biaxially stretched high-density polyethylene and biaxially stretched polypropylene film.

In case the fiber network is a fabric, a knitted network, or a "non-woven", impregnation of the network with thermoplastic material based on an acrylic resin is typically effected with a water-based dispersion. After complete or partial evaporation of the water, the preformed sheet may pass through heated pressure device, including pressure rolls.

Impregnation of unidirectionally aligned fibers with a plastic matrix material can for instance be effected by applying one or more films of the plastic to the top, bottom or both sides of the plane of the fibers and then passing these, together with the fibers, through heated pressure rolls. Preferably, however, the fibers, after being oriented in parallel fashion in one plane, are coated with an amount of a liquid substance containing the plastic matrix material of the monolayer. The advantage of this is that more rapid and better impregnation of the fibers is achieved. The liquid substance may be for example a solution, dispersion or a melt of the plastic. If a solution or a dispersion of the plastic matrix material is used in the manufacture of the monolayer, the process also comprises evaporating the solvent or dispersant, preferably followed by compressing under elevated temperature. Such temperatures and pressures are easily determined by routine experimentation, and typically will be between 70 °C and the melting temperature of the fibers, preferably between 75-135 °C, and between 1 and 100 bar, preferably between 5 and 80 bar, more preferably between 10 and 60 bar.

A special preferred embodiment relates to the use of an aqueous dispersion of the thermoplastic matrix material according to the invention, whereby water is at least partially, preferably for at least 90wt%, more preferably for at least 99wt%, evaporated after application to HPPE fibers whereby these fibers have a strength of at least 3.5 GPa.

The invention further relates to an assembly of at least two preformed sheets according to the invention. The sheets are substantially not linked to one another. With increasing number of preformed sheets, the ballistic protection level is improved, but the weight of the assembly increases, and the flexibility decreases. In order to obtain a maximum flexibility, adjacent sheets in an assembly are preferably not linked to one another. However, to achieve some level of coherence the assembly of preformed sheets may, for example, be stitched through at e.g. the corners. Alternatively the assembly of preformed sheets may be put in a cover or an envelope. Depending on the ballistic threat and the level of protection desired, the skilled person can find an optimum in the number of sheets by some experimentation.

A further embodiment comprises a ballistic-resistant article comprising at least one assembly as defined above.

The invention also relates to a ballistic-resistant article comprising a plurality of preformed sheets according to the invention. Preferably, the ballistic-resistant article comprises a network of fibers comprising a fabric with fibers being highly drawn polyethylene fibers. This embodiment has an Eabs of at least

115 J/kg/m^2 against 9mm*19 Natoball DM11 A1B2 bullet manufactured by MEN, Germany.

Another preferred embodiment relates to a soft ballistic-resistant article comprising a plurality of preformed sheets with unidirectionally aligned highly drawn polyethylene fibers with a strength of at least 3.5 GPa and an acrylic resin in the form of a multiphase (meth)acrylic based polymer dispersion with a first phase having a minimum glass transition temperature of at least 40 °C and a weight average molecular weight of less than 80,000 g/mol and a second phase having a maximum glass transition temperature of 30 °C or less and a weight average molecular weight of more than 100,000 g/mol, the article having an Eabs of at least 180 J/kg/m^2 against 9mm*19 Natoball DM11 A1B2 bullet manufactured by MEN, Germany, and furthermore has a downward deflection of at most 100mm. Preferably this soft ballistic-resistant article has an Eabs of at least 190 J/kg/m^2 and furthermore has a downward deflection of at most 90mm. More preferably this soft ballistic-resistant article has an Eabs of at least 200 J/kg/m^2 and furthermore has a downward deflection of at most 80mm.

The invention further relates to a ballistic-resistant article comprising a plurality of preformed sheets, wherein the network of fibers comprises a fabric, the article further comprising at least two networks of unidirectionally aligned fibers with optionally a matrix. Preferably the fibers in the at least one of the fabric or unidirectionally aligned fibers are polyethylene fibers with a strength of at least 3.5 GPa to achieve a good multi-threat performance and more preferably at least 4.0 GPa. The ballistic resistant article may be in the form of a pressed product, so-called hard ballistics, or in the form of a flexible product, so-called soft ballistics.

The matrix material used in the network of unidirectionally aligned fibers may be an acrylic based thermoplastic material with a glass transition temperature of at least 25 °C according to the invention. Alternatively the preformed sheet of the invention may be combined with a sheet comprising unidirectionally aligned fibers and a matrix. This matrix may comprise another material than the acrilyc based resin. Suitable alternative matrix materials for networks of unidirectionally aligned fibers include thermoplastic and thermosetting materials. Preferably, thermoplastics are applied as matrix material, and particularly suitable are those matrices that can be applied as a dispersion in water. Examples of suitable polymer materials include: acrylates, polyurethanes, modified polyolefins including

SEBS and SIS polymers, as such known in the field of ballistic resistant articles and ethylene vinyl acetate. Preferably, the matrix material contains a polyurethane. More preferably, the polyurethane is a polyetherurethane; that is based on a polyetherdiol, since that provides good performance over a wide temperature range. In a special embodiment, the polyurethane or polyetherurethane is based on aliphatic diisocyanates as this further improves product performance, including its colour stability. The 100% modulus of these plastic matrix materials for unidirectionally aligned fibers is at least 3 MPa. Preferably the 100% modulus is at least 5 MPa. The 100% modulus is generally lower than 500 MPa.

In another preferred embodiment, a suitable alternative matrix material for unidirectionally aligned fibers is Kraton®, applied from an aqueous dispersion. Kraton® polymers comprise a styrene-isoprene-styrene (SIS) triblock copolymer composition with a 100% modulus of 1.4 MPa.

<u>Test Procedures</u>

Anti-ballistic performance, V50 and Eabs were determined at 21°C with test procedures according to Stanag 2920, using 9mm*19 Natoball DM11 A1B2 bullet manufactured by MEN, Germany, in this application measured at test specimen with an areal density of 5.4 km/m2. After conditioning at 21°C and 65% relative humidity during at least 18 hours, an anti-ballistic sample was fixed using flexible straps on a support filed with Roma backing material, which was preconditioned at 35 °C. The kinetic energy of the bullet at V_{50} ($0.5*m_{bullet}*V_{50}^2$) was divided by the total areal density of the armor to obtain a so-called Eabs value. Eabs reflects the stopping power of the armor relative to its weight/thickness thereof. The higher the Eabs value, the better the anti-ballistic performance.

The modulus of the matrix material was determined according to ISO 527. The 100% modulus was determined on film strips with a length of 100 mm (free length between the clamps) and a width of 24 mm. The 100% modulus is the secant modulus measured between strains of 0% and 100%.

Tensile strength (or strength), are defined and determined on multifilament yarns as specified in ASTM D885M, measured at 25 °C using a nominal gauge length of the fiber of 500 mm, a crosshead speed of 50%/min. On the basis of the measured stress-strain curve the modulus is determined as the gradient between 0.3 and 1% strain. For calculation of the modulus and strength, the tensile forces measured are divided by the titre, as determined by weighing 10 metres of fiber; values in GPa are calculated assuming a density of 0.97 g/cm^3.

The glass transition temperatures of the oligomers in the examples use the values in °C determined experimentally using differential scanning calorimetry DSC, taking the peak of the derivative curve as Tg.

Polymer weight average molecular weight of the acrylic thermoplastic material is determined by gel permeation chromatography according DIN 55672, with tetrahydrofuran as solvent at 40 °C, styrene/divinyl bezene as packing material and calibrated using Polystyrene Mp 160-10,000,000 (polymer standard service,PSS) DIN certified as standard.

Intrinsic Viscosity (IV) of UHMWPE is determined according to ASTM D1601, at 135°C in decalin, the dissolution time being 16 hours, with DBPC as anti-oxidant in an amount of 2 g/l solution, by extrapolating the viscosity as measured at different concentrations to zero concentration;

The invention will now further be elucidated by the following example and experiments, without being limited thereto.

Comparative experiment A

A non woven product in the form of a mono-layer was produced from Dyneema® UHMWPE fibers with a strength of 3.5 GPa. For that purpose the Dyneema® fibers were guided over a comb to align them in parallel after which the fibers were wetted with an aqueous dispersion of a matrix material. After drying, the obtained mono-layer contained 33 gram of parallel (unidirectional) aligned UHMWPE fibers and 16 wt% of Kraton® thermoplastic elastomer (polystyrene-polyisoprene-polystyrene block copolymer with a Tg of about -40 °C) as matrix material. Kraton® thermoplastic elastomer is a well-known matrix used for ballistic applications giving the best bullet stopping power. A preformed sheet was produced by stacking 4 monolayers, whereby the fiber direction in adjacent mono-layers were oriented at an angle of 90 degrees, and one Stamylex® linear low-density polyethylene film with a thickness of 7.6 micron (equivalent to an areal density of about 7 g/m^2)) at the outer side of the stack followed by consolidating the stack at a pressure of about 2 MPa and at a temperature of about 130°C.

A flat ballistic-resistant article was made from a loose, non-linked assembly of a number of preformed sheets, the assembly being stitched through at the corners. Ballistic performance for three different assemblies was tested with a bullet type 9mm*19 Natoball DM11 A1B2; V_{50} and Eabs results are given in Table 1. The obtained preformed sheet was cut in strips of 38cm long and 10cm wide and tested on their stiffness by putting one strip on a flat surface and having 16 cm protruding from the table. The downward deflection of the outer most part of the unsupported section of the strip was measured, whereby a higher downward deflection indicates a lower stiffness.

Example I

A mono-layer was produced from Dyneema® UHMWPE fibers with a strength of 3.5 GPa in the same way as for comparative experiment A. In this case a Neocryl® from DSM Neoresins was used as matrix material. After drying, the obtained mono-layer contained 33 gram of parallel (unidirectional) aligned UHMWPE fibers and 16 wt% of Neocryl® (a multiphase (meth)acrylate core/shell copolymer dispersion existign ot two phases, one with a Tg below 30°C and one with a T above 40 °C) as matrix material. A preformed sheet was produced in the same way as Comparative Experiment A by stacking 4 monolayers and one outer Stamylex® linear low-density polyethylene film.

A flat ballistic-resistant article was made from a loose, non-linked assembly of a number of preformed sheets, the assembly being stitched through at the corners. Test results of the ballistic-resistant article as given in table 1. The downward deflection of a preformed sheet is 64mm, which is lower than for experiment A, hence indicating a higher stiffness of the sheets.

Table 1:

Experiment/ Example	Weight [kg/m^2]	V50 [m/s]	Eabs [J/kg/m^2]	Downward deflection [mm]
A	3.3	376	170	137
I	3.3	408	201	64

Table 1 shows that despite the higher stiffness of the sheet according to the invention, a good projectile stopping performance could be reached. This is against the common belief that best projectile stopping performance is achieved with a soft (i.e. not stiff) matrix system and sheets.

CLAIMS

1 Preformed sheet, comprising a network of fibers having a tensile strength of at least 1.5 GPa, impregnated with at least 10% of a plastic material, characterized in that the plastic material comprises a multiphase (meth)acrylic based polymer dispersion with a first phase having a minimum glass transition temperature of at least 40 °C and a weight average molecular weight of less than 80,000 g/mol and a second phase having a maximum glass transition temperature of 30 °C or less and a weight average molecular weight of more than 100,000 g/mol.

2. Preformed sheet according to claim 1, wherein the oligomer has a glass transition temperature of at least 30 ºC below the glass transition temperature of the polymer.

3. Preformed sheet according to claim 1 or claim 2, wherein multiphase polymer dispersion forms a core-shell structure.

4. Preformed sheet according to claim 1 -3, wherein the network of fibers comprises a fabric.

5. Preformed sheet according to claim 1-3 wherein the network of fibers comprises unidirectionally aligned fibers.

6. Preformed sheet according to claim 1-5, wherein the fibers are UHMWPE fibers.

7. Preformed sheet according to claim 1-6, wherein the preformed sheet comprises a separating film on at least one of its outer surfaces.

8. Preformed sheet according to claim 7, wherein the separating film is a biaxially stretched polyolefin film.

9. Assembly of at least two preformed sheets according to any one of the preceding claims, which sheets are substantially not linked to one another.

10. Ballistic resistant article comprising at least one assembly according to claim 9.

11. Ballistic resistant article comprising a plurality of preformed sheets according to claim 2 having an Eabs of more than 115 $J/kg/m^2$ for 9mm*19 Natoball DM11 A1B2 bullets.

12. Ballistic resistant article according to claim 11, further comprising at least two networks of unidirectionally aligned fibers with optionally a matrix.

13. Ballistic resistant article according to claim 12, wherein the matrix for the unidirectional aligned fibers comprises a modified polyolefin, a SIS, or a SEBS.
14. Ballistic resistant article according to claim 12, wherein the matrix for the unidirectional aligned fibers is an acrylic based thermoplastic polymer forming a first phase, further comprising an oligomer in a second phase, wherein the polymer has a glass transition temperature of at least 25 ºC.
15. Use of a plastic material comprising a multiphase (meth)acrylic based polymer dispersion with a first phase having a minimum glass transition temperature of at least 40 °C and a weight average molecular weight of less than 80,000 g/mol and a second phase having a maximum glass transition temperature of 30 °C or less and a weight average molecular weight of more than 100,000 g/mol, in the manufacture of ballistic resistant composites.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/077461

A. CLASSIFICATION OF SUBJECT MATTER
INV. F41H5/04
ADD.

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 practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 987 363 A1 (WACKER CHEMIE GMBH [DE]) 22 March 2000 (2000-03-22) paragraphs [0006] - [0025]; figures 1-3	1-15
A	US 2004/084304 A1 (THOMPSON SAMUEL A [US]) 6 May 2004 (2004-05-06) paragraphs [0024] - [0079]	1-15
A	EP 0 620 410 A1 (ALLIED SIGNAL INC [US]) 19 October 1994 (1994-10-19) column 1, line 42 - column 17, line 29; figure 1	1-15

☐ 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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"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 novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
27 January 2017	03/02/2017

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Kasten, Klaus

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2016/077461

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0987363 A1	22-03-2000	DE 19842661 A1	04-05-2000
		EP 0987363 A1	22-03-2000
		ES 2175882 T3	16-11-2002
		IL 131434 A	12-01-2003
		US 6231921 B1	15-05-2001
US 2004084304 A1	06-05-2004	AU 2003284960 A1	07-06-2004
		CN 1708396 A	14-12-2005
		EP 1558442 A1	03-08-2005
		JP 5329735 B2	30-10-2013
		JP 2006504848 A	09-02-2006
		TW I311593 B	01-07-2009
		US 2004084304 A1	06-05-2004
		WO 2004041529 A1	21-05-2004
EP 0620410 A1	19-10-1994	DE 69419649 D1	02-09-1999
		DE 69419649 T2	27-01-2000
		EP 0620410 A1	19-10-1994
		IL 108894 A	20-11-1997
		US 5354605 A	11-10-1994