EUROPEAN PATENT APPLICATION

(12)

(21) Application number: 93113549.5

(51) Int. Cl.⁵: F41H 5/04

(22) Date of filing: 25.08.93

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(54) Impact resistant helmet.

(57) A penetration resistant article of manufacture having at least one surface defined by a plurality of points at least two of said points located in different horizontal planes, said article comprisng a plurality of prepreg packets each comprising at least two prepreg layers wherein said layers are comprised of a fibrous network in a polymeric matrix wherein said prepreg layers have been precompressed into prepreg packets at a temperature and pressure sufficient to bond adjacent surfaces of adjacent layers.
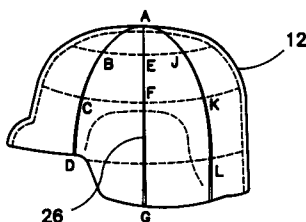
FIG. 3

EP 0 585 793 A1

BACKGROUND OF THE INVENTION

1. Background of the Invention

This invention is in the field of multilayered impact resistant composites and articles of manufacture made from such composites. A more preferred dopant of the invention relates to a helmet comprising an impact resistant composite shell.

2. Prior Art

Composites and helmets having impact resistance, and in particular ballistic impact resistance are known in the art. See for example, G.B. Patent Application No. 2098852; and U.S. Patent Nos. 4,403,012; 4,953,234; 4,457,985; 4,501,856; 4,613,535; 4,199,308; 4,623,574; 4,650,710; 4,309,487; 4,079,161; 4,953,234 and 5,112,667.

SUMMARY OF THE INVENTION

The present invention relates to an impact resistant article of manufacture, such as an helmet, having at least one surface defined by a plurality of points, at least two of said points located in different horizontal planes, said article comprising a plurality of prepreg packets, each comprising at least two pregreg layers wherein said prepreg layers are comprised of a fibrous network in a polymeric matrix such as a woven fabric, non-woven fabric, one or more undirectional fiber networks or a combination thereof and wherein prepreg packets have been precompressed at a temperature and pressure sufficient to bond adjacent surfaces of adjacent layers prior to incorporation in said article.

The impact resistant article of this invention exhibits one or more advantages over conventional impact resistant articles are for example improved impact resistance having the same areal density. As used herein, the "impact resistance" of the article is the resistance to penetration by a designated threat designated the threats include physical objects as for example, a threat, as for example, bullets, fragments, shrapnels and the like, threats also include non-physical objects such as blast from explosion and the like. The impact resistance for designated threats can be expressed by at least three methods: 1. V/50 is the velocity at which 50% of the threats will penetrate the composite while 50% will be stopped by the armor. For composite of equal areal density, which is the weight of the composite panel divided by the surface area, the higher the V/50, the better the resistance of the composite; 2. Total specific energy absorption (SEAT): SEAT is the kinetic energy of the threat divided by the areal density of the composite. The higher the SEAT value, the better the resistance of the composite to the threat; and 3. Striking velocity (V/s) vs. residual velocity (V/r): When a threat strikes an armor panel at a velocity of (V/s), the residual velocity (V/r) is measured after the threat penetrates the composite. The larger the difference between (V/s) and (V/r), the better the resistance to the threat for composite panels of equal areal density. As used herein, the "areal density" corresponds to the weight per unit area of the ballistic resistant armor. In the case of fiber reinforced composites, the ballistic resistance of which depends mostly on filaments, another useful weight characteristic is the fiber areal density of the composite. This term corresponds to the weight of the filament reinforcement per unit area of the composite (AD).

It is believed that the improved impact resistance results from the precompression of the prepreg packets prior to incorporation of the prepreg packets into the article. The improvement in impact resistance is especially apparent when the fibrous network is a woven or non-woven fabric especially against light or ballistic projectiles as for example 2 grain fragments.

BRIEF DESCRIPTION OF THE DRAWINGS

This invention will be more fully understood and further advantages will become apparent when reference is made to the following detailed description of the invention and the accompanying drawings in which:

Figure 1 is the top view of a helmet of the present invention.

Figure 2 is the side view of a helmet of the present invention.

Figure 3 is the side view of a helmet of the present invention showing a prepreg packet.

Figure 4 is a schematic and break away view of a helmet of the present invention showing fiber direction in the prepreg layers.

Figure 5 is a cross-section of a portion of the helmet shell showing the prepreg packets.

Figure 6 is a cross-section of a portion of a prepreg packet showing the prepreg layers.
Figures 7 and 8 are not to scale drawings of a prepreg packet cut into a pattern useful to make the shell of the helmet of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention will be understood by those skilled in the art by reference to the accompanying drawings. While the preferred embodiments of the present invention are described with reference to the accompanying Figures 1-8, these Figures illustrate only a preferred embodiment and should not limit the scope of the present invention.

The present invention is directed to a non-planar composite article as for example a helmet identified in figures 1 and 2 by the numeral 10. Helmet 10 comprises an impact resistant composite shell 12 comprises a plurality of prepreg packets 14. The helmet of the present invention requires at least two prepreg packets 14. The total number of prepreg packets 14 will vary widely depending on the uses of the article. In general, the greater the number of prepreg packet 14 interfaces the lower the penetration resistance of the article. Therefore, where improved impaction resistance is desired, it is desirable to minimize the number of packet interfaces by minimizing the number of prepreg packets 14. This is balanced against the weaknesses at the seams if there are too few layers. Depending upon the materials used, and the amount of protection needed, this balance can be optimized with routine experimentation.

Composite shell 10 is preferably made of at least about 5, more preferably from about 5 to about 30 and most preferably from about 5 to 20 prepreg packets 14.

Prior to incorporation into the article of this invention, prepreg packets 14 are individually precompressed at a temperature and pressure sufficient to bond the surfaces of adjacent layers to each other. The requirement that the individual prepreg packets 14 are precompressed is critical to the enhanced impact resistance of the article of this invention. Surprisingly, it has been discovered that use of precompressed prepreg packets 14 in the construction of the article results in enhanced impact resistance. This is especially true for fabric impact resistant articles which heretofore have exhibited reduced penetration resistance, especially against lower grain projectiles. Preferably, the prepreg packets are precompressed at a temperature equal to or less than about 80°C and at a pressure equal to or less than about 40 MPa. Useful precompression temperatures and pressures are preferably from about 20°C to about 70°C and from about 5 MPa to about 40 MPa, respectively, and are most preferably from about 40°C to about 60°C and from about 7 to about 30 MPa, respectively.

Helmet 10 maximizes the advantage of having precompressed prepreg packets 14 comprised of prepreg layers 16 form from a fibrous network as for example a woven or non-woven fabric or unidirectional fiber construction, embedded in a polymer matrix. Such a construction results in improved impact resistance. As shown in the figures, in the preferred embodiments of the invention a fabric, especially a woven fabric, is embedded in the matrix. Helmet 10 has a plurality, at least about 2, preferably at least about 5 packets and most preferably about 5 to 20 prepreg packets 14 cut into patterns 22 such as shown in Figures 7 and 8. It is desirable to maximize the number of layers 16 in each packet 14 and minimize the number of packets 14. This is done to the extent that packets 14 do not become so thick that unacceptable wrinkles develop, or cuts 24 result in seams which result in unacceptable weaknesses in the helmet. Pattern 22 contain cuts such as cut 24 which remove excess material to enable pattern 22 to take a three-dimensional shape and have the cut portions having edges 26 which substantially close up to form seams 26 when pattern 22 is formed into a shell 12. The shell 12 is built by a plurality of prepreg packets 14. The seams of adjacent packets 14 are located so as not to overlap. Figures 7 and 8 show two different patterns 22 used to avoid overlapping of seams 26 in two packets 14.

The remaining material between cuts 24 are lobes 30. Although Figures 7 and 8 show a preferred pattern 22 having eight lobes 30, it should be appreciated that the number of lobes 30 can be varied widely depending on a number of factors as for example the shape of the article. Individual lobe 31 shows a schematic illustration of the preferred woven fabric fiber network in adjacent layers 32 and 33 which had been built up to form packet 14 that had been cut into pattern 22. A plurality of patterns 22 can be "laid-up", that is placed upon one another and put into a suitable means to shape it into shell 12. This can be done by a compression type mold or a stamping mold. The helmets can also be molded in an autoclave. The helmets are preferably compression molded onto a suitable mold. Depending upon the material, molding parameters such as time, temperature and pressure, can vary. For example, a most preferred set of conditions for molding a helmet 10 having a surface area of approximately 1.29 ft^2 (0.12 m^2) made using extended chain polyethylene fiber is at a pressure of from about 30 to about 90 tons (27,000 Kg to 82,000 Kg), at a temperature of from about 80°C to about 130°C for from about 5 minutes to about 90 minutes

and preferably about 10 minutes to about 45 minutes.

Fibers for use in the fabrication of layers 16 may vary widely and may be organic or inorganic fibers. For the purposes of the present invention, fiber is an elongated body, the length dimension of which is much greater than the transverse dimensions of width and thickness. Accordingly, the term fiber includes monofilament fiber, multifilament fiber, ribbon, strip, a plurality of any one of combinations thereof and the like having regular or irregular cross-section. The fibers may be twisted or have zero twist. Depending on the application for use of the prepreg layer in the multilayer composite of the present invention different fibers and different matrices can be used.

Essentially any fiber made of a wide range of materials and having a wide range of tensile and other properties may be used in the practice of this invention . Preferred fibers for use in the practice of this invention are those having a tenacity equal to or greater than about 7 grams/denier (g/d), a tensile modulus equal to or greater than about 50 g/d and an energy-to-break equal to or greater than about 30 joules/grams. The tensile properties are determined by an Instron Tensile Tester by pulling the fiber at 10 in (25.4 cm) fiber length, clamped in barrel clamps at 10 in/min (25.4 cm/min). Among these particularly preferred embodiments, most preferred are those embodiments in which the tenacity of the fiber are equal to or greater than about 15 g/d, the tensile modulus is equal to or greater than about 300 g/d, and the energy-to-break is equal to or greater than about 20 joules/grams. In the practice of this invention, fiber of choice have a tenacity equal to or greater than about 19 g/d, the tensile modulus is equal to or greater than about 1300 g/d and the energy-to-break is equal to or greater than about 40 joules/grams.

The denier of the fiber may vary widely. In general, fiber denier is equal to or less than about 4000. In the preferred embodiments of the invention, fiber denier is from about 10 to about 4000, the more preferred embodiments of the invention fiber denier is from about 10 to about 2600 and in the most preferred embodiments of the invention, fiber denier is from about 10 to about 1300.

The fiber may be formed from inorganic or organic materials. Useful inorganic fibers may vary widely. Illustrative of such fibers are glass (S-glass, E-glass, etc) fibers, boron fibers, silicone carbide fibers, graphite fibers and the like.

Useful organic fibers may vary widely. Illustrative of useful organic fiber are those composed of thermosetting resins and thermoplastic polymers such as polyesters; polyolefins; polyetheramides; fluoropolymers; polyethers; celluloses; phenolics; polyesteramides; polyurethanes; epoxies; aminoplastics; polysulfones; polyetherketones; polyetherether-ketones; polyesterimides; polyphenylene sulfides; polyether acryl ketones; poly(amideimides); polyimides; aramids (aromatic polyamides), such as poly(2,2,2-trimethyl-hexamethylene terephthalamide) (Kevlar)and the like; aliphatic and cycloaliphatic polyamides, such as polyhexamethylene adipamide (nylon 66), polycaprolactam (nylon 6)and the like; and aliphatic, cycloaliphatic and aromatic polyesters such as poly (1,4-cyclohexlidene dimethylene terephathalate) cis and trans, poly(ethylene terephthalate) and the like. Also illustrative of useful organic filaments are those of liquid crystalline polymers such as lyotropic liquid crystalline polymers which include polypeptides such as poly-benzyl L-glutamate and the like; aromatic polyamides such as poly(1,4-benzamide), poly(4,4'-biphenylene 4,4'-bibenzo amide), poly(1,4-phenylene 4,4'-terephenylene amide), poly(1,4-phenylene 2,6-naphthal amide), and the like; polyoxamides such as those derived from 2,2' dimethyl-4,4'diamino biphenyl, chloro-1,4-phenylene diamine and the like; polyhydrazides such as poly chloroterephthalic hydrazideand the like;poly(amide hydrazides such as poly(terephthaloyl 1,4 amino-benzhydrazide) and those prepared from 4-amino-benzhydrazide, oxalic dihydrazide, terephthalic dihydrazide and para-aromatic diacid chlorides; polyesters such as poly(oxy-trans-1,4-cyclohexyleneoxycarbonyl-trans-1,4-cyclohexylenecarbonyl-trans-β,4-phenyleneoxyterephthaloyl),poly(oxy-trans-1,4-cyclohexylene-oxycarbonyl-tran s-1,4-cyclohexylenecarbonyl-β-oxy-(2-methyl 1,4-phenylene)oxy-terephthaloyl)] ,and the like; polyazomethines such as those prepared from 4,4'-diaminobenzanilide and terephthalaldephide, methyl-1,4-phenylenediamine and terephthalaldelyde and the like; polyisocyanides such as poly(-phenyl ethyl isocyanide), poly(n-octyl isocyanide) and the like; polyisocyanates such as poly (n-alkyl isocyanates) as for example poly(n-butyl isocyanate), poly(n-hexyl isocyanate) and the like; lyotropic crystalline polymers with heterocyclic units such as poly(1,4-phenylene-2,6-benzobisoxazole)(PBO), poly(1,4-phenylene-1,3,4-oxadiazole), poly(1,4-phenylene-2,6-ben-zobisimidazole), poly[2,5(6)-benzimidazole] (AB-PBI), poly[2,6-(1,4-phneylene)-4-phenylquinoline], poly[1,1'-biphenylene)-6,6'-bis(4-phenylquinoline)] and the like; polyorganophosphazines such as polyphosphazine, polybisphenoxyphosphazine, poly]bis(2,2,2'trifluoroethyelene) phosphazine and the like; metal polymers such as those derived by condensation of trans-bis(tri-n-butylphosphine)platinum dichloride with a bisacetylene or trans-bis(tri-n-butylphosphine)bis(1,4-butadinynyl) platinum and similar combinations in the presence of cuprous iodine and an amide; cellulose and cellulose derivatives such as esters of cellulose as for example triacetate cellulose, acetate cellulose, acetate-butyrate cellulose, nitrate cellulose, and sulfate cellulose, ethyl ether cellulose, hydroxypropyl ether cellulose, carboxymethyl ether cellulose, ethyl hydrox-

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yethyl ether cellulose, cyanoethylethyl ether cellulose, acetoxyethyl ether cellulose , benzoyloxypropyl ether cellulose, phenyl urethane cellulose and the like; thermotropic copolyesters as for example copolymers of 6-hydroxy-2-naphthoic acid and p-hydroxy benzoic acid, copolymers of 6-hydroxy-2-naphthoic acid, terephthalic acid and p-amino phenol, copolymers and 6-hydroxy-2-naphthoic acid, terephthalic acid and hyudroquinone, copolymers of 6-hydorxy-2-naphtoic acid, p-hydroxy benzoic acid, hydroquinone and terephthalic acid, copolymers of 2,6-naphthalene dicarboxylic acid, terephthalic acid, isophthalic acid and hydroquinone, copolymers of 2,6-napthalene dicarboxylic acid and terephthalic acid, copolymers of p-hydroxybenzoic acid, terephthalic acid and 4,4'-dihydroxydiphenyl, copolymers of p-hydroxybenzoic acid, terephthalic acid, isophthalic acid and 4,4'-dihydroxydiphenyl, p-hydroxybenzoic acid, isophthalic acid, hydroquinone and 4,4'-dihydroxybenzophenone, copolymers of phenylterephthalic acid and hydroquinone, copolymers of chlorohydroquinone, terephthalic acid and p-acetoxy cinnamic acid, copolymers of chlorophydroquinone, terephthalic acid and ethylene dioxy-4,4'-dibenzoic acid, copolymers of hydroquinone, methylhydroquinone, p-hydroxybenzoic acid and isophthalic acid, copolymers of (1-phenylethyl)hydroquinone, terephthalic acid and hydroquinone, and copolymers of poly(ethylene terephthalate) and p-hydroxybenzoic acid; and thermotropic polyamides and thermotropic copoly(amide-esters).

In the preferred embodiments of the invention the fiber used to form the fabric are organic fibers. Preferred organic fibers include a polyethylene fiber (preferably of high molecular weight), nylon 6 or nylon 66 fiber (preferably nylon 6 and nylon 66 and more preferably nylon 6), an aramid fiber, polyester fiber, a fiber formed from liquid crystalline polymers such as liquid crystalline copolyester and mixtures thereof. These fibers and methods for their preparation are known to those of skill in the art. For example, suitable poly (ethylene) fibers and methods for their preparation are described in U. S. Patent Nos. 4,457,985; 4,551,296; 4,137,394; and 4,356,138; German Off. 3,004,699; GB 2051667; and EPA 64,167. Such fibers can be obtained commercially as for example from Allied Signal Inc. under the trade name Spectra® polyethylene fibers.

Suitable aramid fibers are those formed principally from aromatic polyamide. Such fibers and their method of preparation are described in U.S. Patent No. 3,671,542. Such fibers as for example poly-(phenylene terephthalamide) fibers and poly(metaphenylene isophthalamide) fibers are produced commercially by Dupont Corporation under the trade names Kevlar® 29, 49, 129 and 149 and under the trade name Nomex®, respectively. In the case of liquid crystal copolyesters, suitable fibers are disclosed, for example, in U.S. Patent Nos. 3,975,487; 4,118,372; and 4,161,470.

The number of fiber ends in layers 16 is not critical and may vary widely. Prepreg layers 16 of the present invention preferably contain from about 5 to about 30 fiber ends per inch (1.57 to 12 fiber ends/cm) and more preferably about 10 to about 20 per inch (2.4 to 9.4 fiber ends/cm). Each layer 16 is preferably from about 0.0001 in. (2.54×10^{-10} cm) to about 0.04 in. (0.1 cm), preferably about 0.0005 in. (0.0013 cm) to about 0.01 in. (0.035 cm), more preferably about 0.0005 in. (0.0012 cm) to about 0.03 in. (0.08 cm) and most preferably 0.0005 (0.0012 cm) to 0.02 in (0.05 cm) thick. Layers having these dimensions are particularly useful when made of extended chain polyethylene having a yarn of about 1200 denier/118 filaments. The areal density is used to indicate the amount of fiber and/or resin per unit area of the prepreg layer. It is determined by the number of yarn strands laid per unit width of prepreg sheet and the amount of resin applied to the yarn. Typically if a 1200 denier/118 filament yarn is laid by 15 ends per inch (6 ends/cm) the yarn areal density in the prepreg sheet would be about 79 grams per square meter.

Layers 16 comprise a fiber network (which can have various configurations) embedded or substantially embedded in a polymeric matrix which preferably substantially coats each filament contained in the fiber bundle and packet 14 comprises a plurality of such layers 16. Layers 16 may be formed by any suitable method and fabricated into packet 14 by any such method. For example, a plurality of filaments can be grouped together to form a twisted or untwisted yarn bundles in various alignment. The fibers may be formed as a felt, knitted or woven (plain, basket, satin and crow feet weaves, etc.) into a network, fabricated into non-woven fabric, arranged in parallel uniaxial array, layered, or formed into a woven or nonwoven fabric by any of a variety of conventional techniques and dispersed in the matrix employing any suitable technique as for example melt blending the fibers in a melt of the polymer, solution blending the fibers in a solution of the polymer followed by removal of the solvent and consolidation of the polymer coated fibers, polymerization of monomer in the presence of the fiber and the like and thereafter aligning the layers 16 in the desired arrangement to impregnated a woven or non-woven fabric with the desired polymer matrix material and thereafter form packets 14. One such procedure involves aligning the desired number of layers 16 preferably at least two adjacent coplanar prepreg layers 16. Thereafter the aligned layers 16 are molded at a suitable temperature and pressure to form a prepreg packet 14 of the desired thickness. Another suitable procedure is where the fiber network is formed of a plurality of uniaxial layers in which fibers are aligned substantially parallel and undirectionally such as in a prepreg, pultruded sheet and the like which

are fabricated into a laminate packet 14 comprised of a plurality of such uniaxial layers in the which polymer forming the matrix coats or substantially coats the filaments of multi-filament fibers and the coated fibers are arranged in a sheet-like array and aligned parallel to another along a common fiber direction. Successive uniaxial layers 16 of such coated, unidirectional fibers can be rotated with respect to previous layer 16 to form a laminated fibrous packet 14. An example of such laminate fibrous packet 14 are composites with the second, third, fourth and fifth uniaxial layers 16 are rotated +45°, -45°, 90° and 0°, with respect to the first layer, but not necessarily in that order. Other examples include composites with 0°/90° layout of fibers in adjacent uniaxial layers. The laminated packet 14 composed of the desired number of uniaxial layers 16 can be precomprised at a suitable temperature and pressure to form a packet 14 having a desired thickness. Useful techniques for forming fiber networks embedded in a polymeric matrix for ballistic resistance applications include those variations commonly employed in the preparation of aramid and polyethylene fabrics and unidirectional prepregs and for consolidating same into for ballistic-resistant articles. For example, the techniques described in U.S. Patent Nos. 4,181,768; 4,916,000; 4,650,710; 4,681,792; 4,737,401; 4,543,286; 4,563,392; 3,971,072; 3,988,780; 4,183,097; 3,855,632; 4,522,871; 4,510,200; 4,501,856; 4,623,574; 4,748,064; 4,457,985 and 4,403,012; PCT WO/91/08895; and M.R. Silyquist et al., J. Macromol Sci. Chem., A7(1), pp. 203 et. seq. (1973) are particularly suitable. In the preferred embodiments of the invention, shell 12 is formed of layers of woven or non-woven fabrics and in the more preferred embodiments of the invention are formed of woven fabrics.

Wetting and adhesion of fibers in the polymer matrices, is enhanced by prior treatment of the surface of the fibers. The method of surface treatment may be chemical, physical or a combination of chemical and physical actions. Examples of purely chemical treatments are used of SO_3 or chlorosulfonic acid. Examples of combined chemical and physical treatments are corona discharge treatment or plasma treatment using one of several commonly available machines.

The matrix material may vary widely and may be formed of any thermoplastic polymer,thermosetting resin or a mixture thereof. Suitable polymeric matrix materials include those mentioned below for use in the formation of the fibers of layer 12. Useful matrix polymer materials may exhibit relatively high e.g.equal to or less than about 500 psi (3450 kPa) or may exhibit relatively high modulus e.g. greater than about 500 psi (3450 k Pa). It has been found that a helmet made of a lower modulus matrix material, such as one having lower ASTMD-638 tensile modulus such as a modulus of less than about 20,000 psi (138 MPa), preferably less than about 6,000 psi (41 MPa), is more resistant to a delamination of layers upon ballistic impact than a helment made using a matrix polymer having a high tensile modulus matrix material such as black copolymers of conjugated arenes and vinyl aromatic monomers. However, helmets made using lower modulus materials are not as stiff or rigid as helmets made using high modulus materials, i.e., a tensile modulus greater than 6,000 psi (41 MPa) preferably greater than about 20,000 psi (138 MPa) such as blends of one or more thermoplastic polymers as for example polyurethane and one or more thermosettung resisns such as a vinyl ester. Accordingly, the present invention includes a Composite, and helmet made of a composite, having separate layers made using different matrix materials in the different layers. Higher modulus matrix materials are used to provide rigidity and lower modulus matrix to resist delamination. Preferably, the composite has one or more of the higher modulus matrix resin containing layers on at least one surface and optionally both outer surfaces. In the application for use in a helmet, the composite is designed so that there is at least one and preferably at least two prepreg packets having higher modulus matrix material on the outside of the helmet. There is at least one and preferably at least two lower modulus matrix material containing prepreg packets on the inside of the composite. This provides a helmet having rigidity and lamination resistance.

In one preferred embodiments of the invention the matrix material is a relatively high modulus blend of one or more thermoplastic polymers and one or more thermosetting resins. The choice of thermoplastic polymer and thermosetting resin and their relative amounts may vary widely depending on the desired characteristics of the composite. Useful matrix materials are described in more detail in WO 91/08895 and are preferably a mixture of thermosetting vinyl ester resin and a thermoplastic polyurethane.

In another preferred embodiment of this invention the matrix material is selected from the group consisting of relatively low modulus elastomeric materials. A wide variety of elastomeric materials and formulation may be utilized in the preferred embodiments of this invention. Representative examples of suitable elastomeric materials for use in the formation of the matrix are those which have their structures, properties, and formulation together with cross-linking procedures summarized in the Encyclopedia of Polymer Science, Volume 5 in the section Elastomers-Synthetic (John Wiley & Sons Inc., 1964)and those which are described in U.S. Patent No. 4,916,000 and are preferably block copolymers of conjugated dienes such as butadiene and isoprene are vinyl aromatic monomers such as styrene, vinyl toluene and t-butyl styrene are preferred conjugated aromatic monomers. Block copolymers incorporating polyisoprene may be

hydrogenated to produce thermoplastic elastomers having saturated hydrocarbon elastomer segments. The polymers may be simple tri-block copolymers of the type A-B-A, multiblock copolymers of the type (AB)n (n = 2-10) or radial configuration copolymers of the type R-(BA)x (x = 3-150); wherein A is a block from a polyvinyl aromatic monomer and B is a block from a conjugated dien elastomer. Many of these polymers are produced commercially by the Shell Chemical Co. and described in the bulletin "Kraton Thermoplastic Rubber", SC-68-81.

The volume ratios of resin to fiber may vary. In general, the ratio is equal to about 5 volume % up to about volume % based on the total volume of the resin and fiber. In the preferred embodiments of the invention, the ratio is from about 5 volume % to about 70 volume %, the more preferred embodiments of this invention is from about 10 volume % to about 50 volume % and the most preferred embodiments of this invention is from about 15 volume % to about 40 volume %.

Composites made using packets 14 are made using the above-described packets 14. One technique for forming a composite includes the steps of arranging the desired number of prepreg layers 16 and precompressing them to form a packet 14 having at least precompressed 2 layers, and preferably from 2 to about 500 layers, more preferably 40 to 150 precompressed layers and most preferably 60 to 120 precompressed layers. The composite is made by laying up the desired number of packets 14 to form a precomposite, after which the precomposite is heated under pressure to cause the matrix material to flow and occupy any void spaces to form the composite. Suitable means include compression molding, stamping, or heating under pressure within an autoclave. In the above cases, it is possible that the matrix can be caused to stick or flow without completely melting. In general, if the matrix material is caused to melt, relatively little pressure is required to form the composite; while if the matrix material is only heated to a sticking point, generally more pressure is required. Also, the pressure and time to set the composite and to achieve optimal properties will generally depend on the nature of the matrix material (chemical composition as well as molecular weight) and processing temperature.

The non-planar penetration resistant article of this invention has many uses. For example, the article can be a protective helment as for example a military helment, a motorcycle helmet and the like. The article can be other non-planar articles such as a radar dome for aircraft, and penetration resistant parts for airplanes, helicopters and military vehicles.

The following examples are set forth below to illustrate the nature of the invention and method of carying it out. However, the invention should not be considered limited to the details thereof.

EXAMPLE 1

This example illustrates the procedures for fabrication of a military helmet using modified PASGT type mold of medium size. The standard PASGT mold of medium size has a wall thickness of 0.345" (0.88 cm), which was modified and enlarged to a wall thickness of 0.40" (1 cm) to accommodate a shell weight of 2.55 lbs. (1.16 Kg). Figs. 1 and 2 show the general view of this type of helmet shell.

The helmet shell was made from 36 resin coated Spectra®-900 fabric layers. Spectra®-900 fabric is woven from Spectra® yarn which is extended chain polyethylene yarn produced by Allied-Signal Inc. Spectra®-900 yarn has a tenacity of approximately 29 gms/denier, a modulus of approximately 1250 grams/denier, and an energy to break of approximately 55 Joules/denier, a yarn denier of approximately 1200/118 filaments and an individual denier per filament of 10. Two types of Spectra® fabric were prepared: S-904 and S-903. Styles S-904 and S-904 are both woven from Spectra®-900 yarns, however, S-903 was a tighter woven fabric with 7 oz/sq. yard (238 g/m^2) as compare to S-904 of 6 oz/sq. yard (204 g/m^2). Style S-904 fabric, 82% by weight, was corona treated and coated with, 18%, uncured thermoset vinylester resin. The corona treatment improved the interfacial adhesion between Spectra® fabric and vinylester resin. Vinylester resin was chosen becaue of its hardness which was suitable for exterior surfaces of the shell to prevent possible denting due to impact. Style S-903 fabric was coated first with uncured thermoset vinylester and subsequently with thermoplastic urethane. The weight ratio of fabric/vinylester/urethane was 80/10/10 and this double coated fabric was suitable for interior uses because urethane is an adhesive material and the adding of urethane will also improve the ballistic impact due to its elastic behavior. All of these resin coated fabric were cut into 21" (53 cm) x 21" (53 cm) squares with the exception of two 12" diameter (305 cm) circular crown patches. The crown patch was used to compensate any thickness variations introduced during stamping of the 6-lobes configuration. The novel feature of this invention is to pre-compress numerous resin coated fabric layers (21" (53 cm) x 21" (53 cm) squares), for instance 6 layers, together to form a ply under a pressure of 130 tons/sq. ft. (1.27 x 10$_6$ kg/m^2) at room temp. for 5 minutes. Each ply was then cut into either "A" or "B" pattern as shown in FIGs. 7 and 8. The starting sequence of hand layup of the fabric layer, plies, and circular crown patches on the core (male) mold is

shown in the following table.

Table

Layer No.	Lobe pattern	fabric type	resins resins	No. of layers pre-compressed
1	A	S-903	PU/VE	None
2 to 7	B	-	-	6
8 to 13	A	-	-	6
14	12" (30 cm) diameter	-	-	None
15 to 20	B	-	-	6
21	12" (30 cm) diameter	-	-	None
22 to 27	A	-	-	6
28 to 31	B	-	-	4
32 to 34	21" (53 cm) diameter	S-904	VE	3
35	B	-	-	None
36	A	-	-	None

The layers from 2 to 7, 8 to 13, 15 to 20, 22 to 27 (6 layers), 28 to 31 (4 layers), 32 to 34 (3 layers), were, respectively, pre-compressed plies of either "A" or "B" patterns as shown in the above table.

After all of the above layers, plies and circular patches, were draped over the core of the mold which was heated to about 110° C, the mold was closed under 200 tons (1.8 x 10$_6$ kg) of pressure for 20 minutes to cure the vinylester/polyurethane resin matrix. The stamped shell was then removed from the mold and was edge trimmed and weighed 2.53 lbs. (1.15 kg). The shell has an average wall thickness of approximately 0.42" (1.07 cm).

Ballistic performance of this shell was evaluated at H. P. White Laboratory, Inc. Firings were conducted in accordance with the general requirements of MIL-STD-662E using designated fragment simulators. The V/50 was 4,249 ft/sec (1,295 m/sec). V/50 is the velocity at which at least 50% of the fragments are stopped by the target. The computed total specific energy absorption (SEAT) is 11.2 Joule-sq. meter/kg.

Example 2

Example 1 was repeated with the exception that, instead of precompression of numberous layers into plies, the shell was fabricated from 36 single resin coated fabric layers as shown in the table of Example 1. The shell weight was 2.56 lbs. (1.16 kg) and the measured V/50 and computed (SEAT) are 4,084 ft/sec (1,245 m/sec) fps and 10.3 Joule-sq. meter/kg., respectively.

Claims

1. A penetration resistant article of manufacture having at least one surface defined by a plurality of points at least two of said points located in different horizontal planes, said article comprising a plurality of prepreg packets each comprising at least two prepreg layers wherein said layers are comprised of a fibrous network in a polymeric matrix wherein said prepreg layers have been precompressed at a temperature and pressure sufficient to bond adjacent surfaces of adjacent layers.

2. A penetration resistant article as recited in claim 1 which is a helmet.

3. The helmet as recited in claim 2 wherein the prepreg packets are flat and are cut into patterns to enable the prepreg packet to be formed into the shape of the shell, and the cuts in the pattern being made so that upon being formed into the shape of the shell the prepreg packets having substantially no wrinkles with the cuts having adjacent edges which substantially come together to form a seam, adjacent prepreg packets having seams which do not overlap.

4. The helmet as recited in claim 2 wherein the prepreg layer comprises an array of at least two adjacent coplanar fibrous elements, with each element comprising a fabric embedded in a polymeric matrix, the adjacent elements connected by the polymer matrix.

5. The helmet as recited in claim 2 wherein the fibers have a tensile modulus of at least about 40 g/denier and an energy to break of at least 7 J/gram.

6. The helmet as recited in claim 5 wherein each prepreg packet comprises 5 or more prepreg layers.

7. The helmet as recited in claim 2 wherein the composite shell comprises from 2 to 50 prepreg packets.

8. The helmet as recited in claim 2 wherein the fiber is selected from the group consisting of polyethylene, nylon, polyester, polyaramid, and combinations thereof.

9. The helmet as recited in claim 3 wherein the angle of fiber in alternate prepreg layers of a prepreg packet is substantially the same.

10. The helmet as recited in claim 2 wherein the tensile modulus of the polymeric matrix of at least two of the prepreg packets is different.

11. The helmet as recited in claim 9 wherein the shell has an inside and an outside and wherein the shell comprises at least the two outer prepreg packets having a polymer matrix with a higher tensile modulus than the polymer matrix of the other layers of the shell.
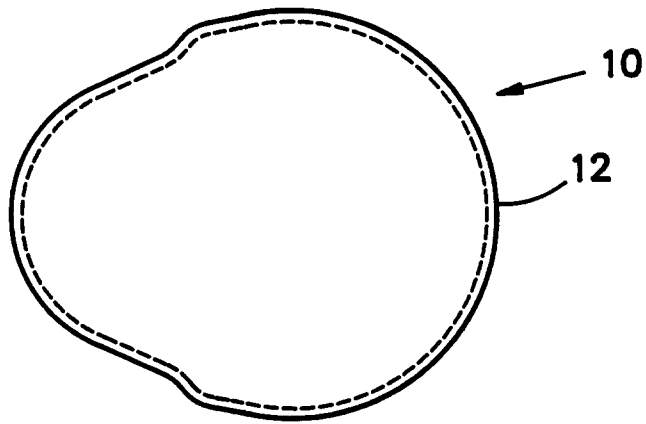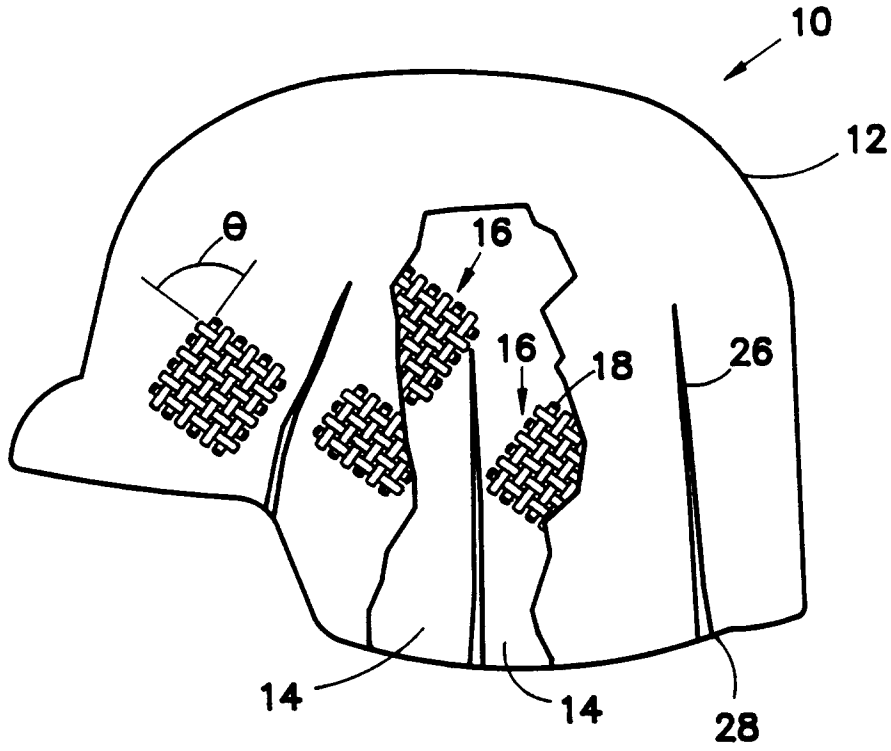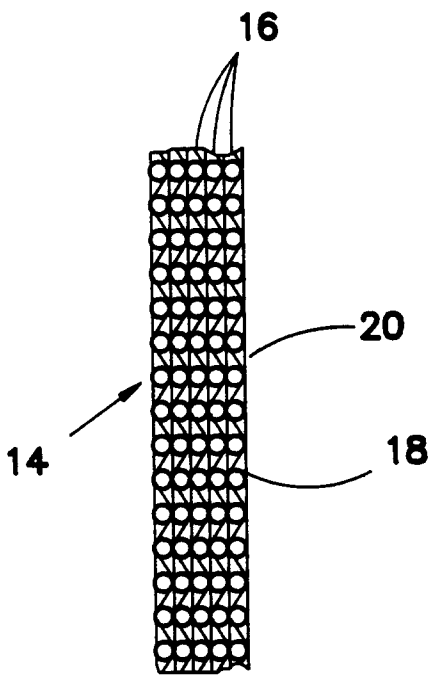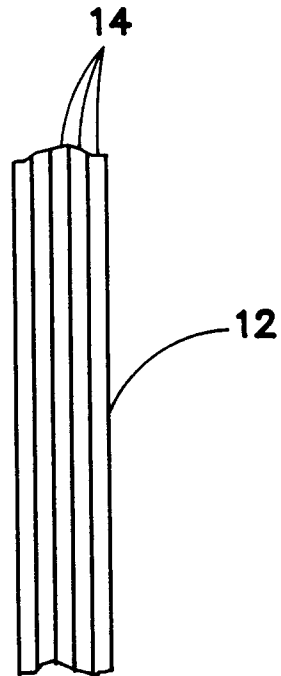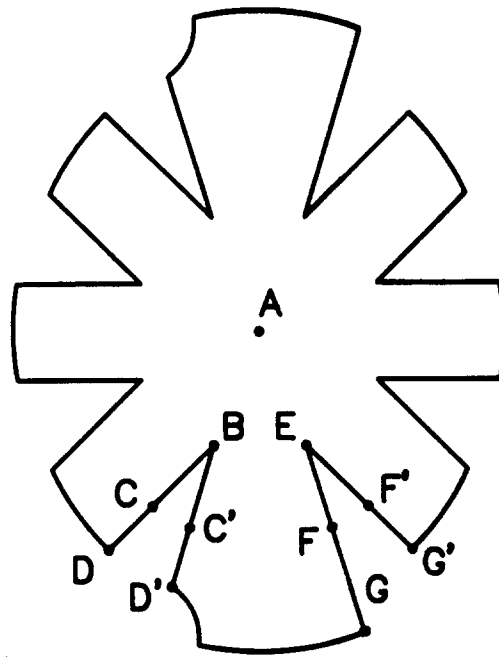
FIG. 1
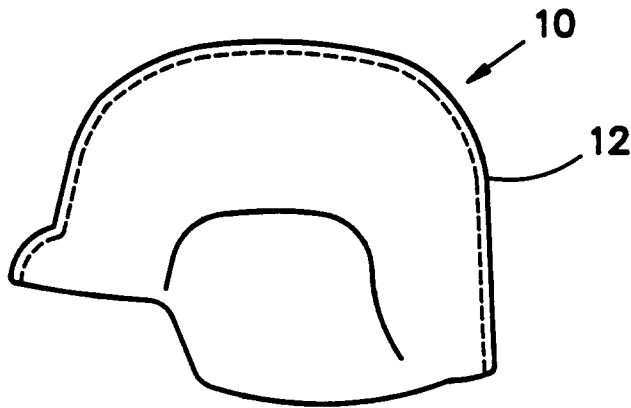
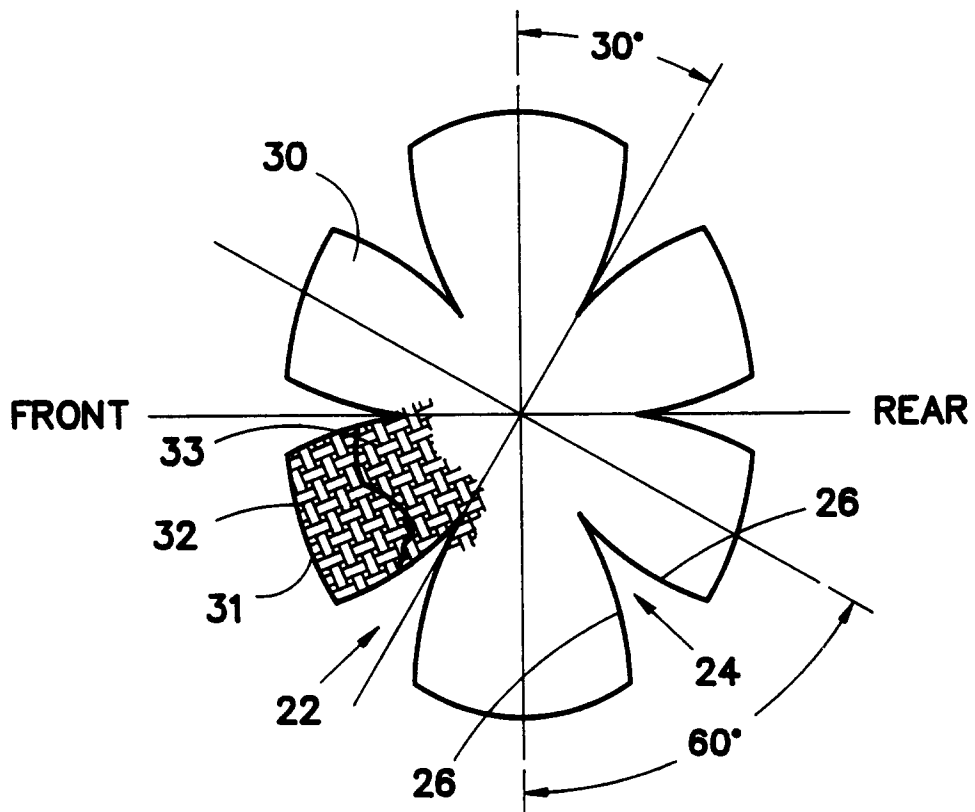FIG. 2
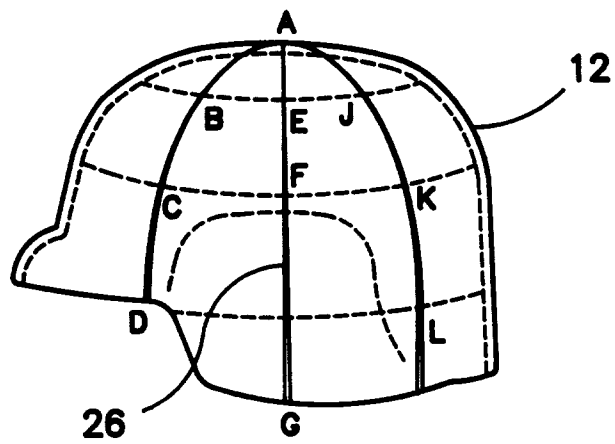
FIG. 3

FIG. 4

FIG. 5

FIG. 6

FIG. 7

FIG. 8

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
Y,D	US-A-5 112 667 (H.L.LI) * the whole document * ---	1-11	F41H5/04
Y,D	US-A-4 309 487 (R.R.HOLMES) * column 3, line 27 - line 41 * ---	1-11	
A,D	US-A-4 953 234 (H.L.LI) * the whole document * ---	1-11	
A,D	US-A-4 613 535 (G.A.HARPELL) ---	1	
A,D	US-A-4 748 064 (G.A.HARPELL) -----	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.5)
			F41H

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	7 December 1993	Triantaphillou, P

EPO FORM 1503 03.82 (P04C01)