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(54) POLYMERIC BALLISTIC MATERIAL AND (52) U.S. Cl. .... 428/36.9; 428/218  
METHOD OF MAKING

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(57) ABSTRACT

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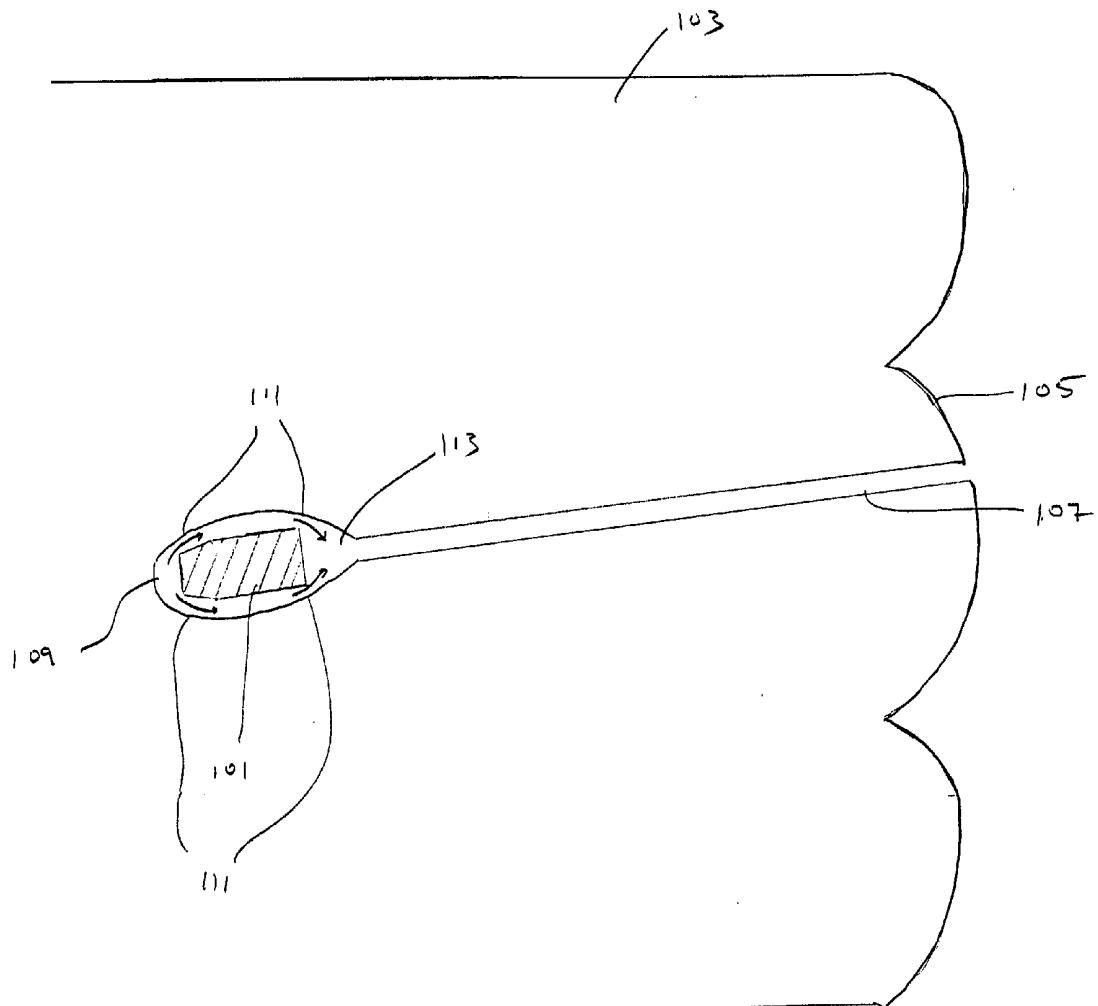
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This invention relates to a polymeric ballistic material comprising a high molecular weight, high density polyethylene (HMW-HDPE) and/or composite, and to articles made from this ballistic material suitable for stopping projectiles. The articles may include backstops for firing ranges and home use, armor for vehicles, personnel, and aircraft, training targets, protection for temporary or mobile military and/or police installations, buildings, bunkers, pipelines or any "critical" need equipment that might require protection from ballistic impact, and the like.



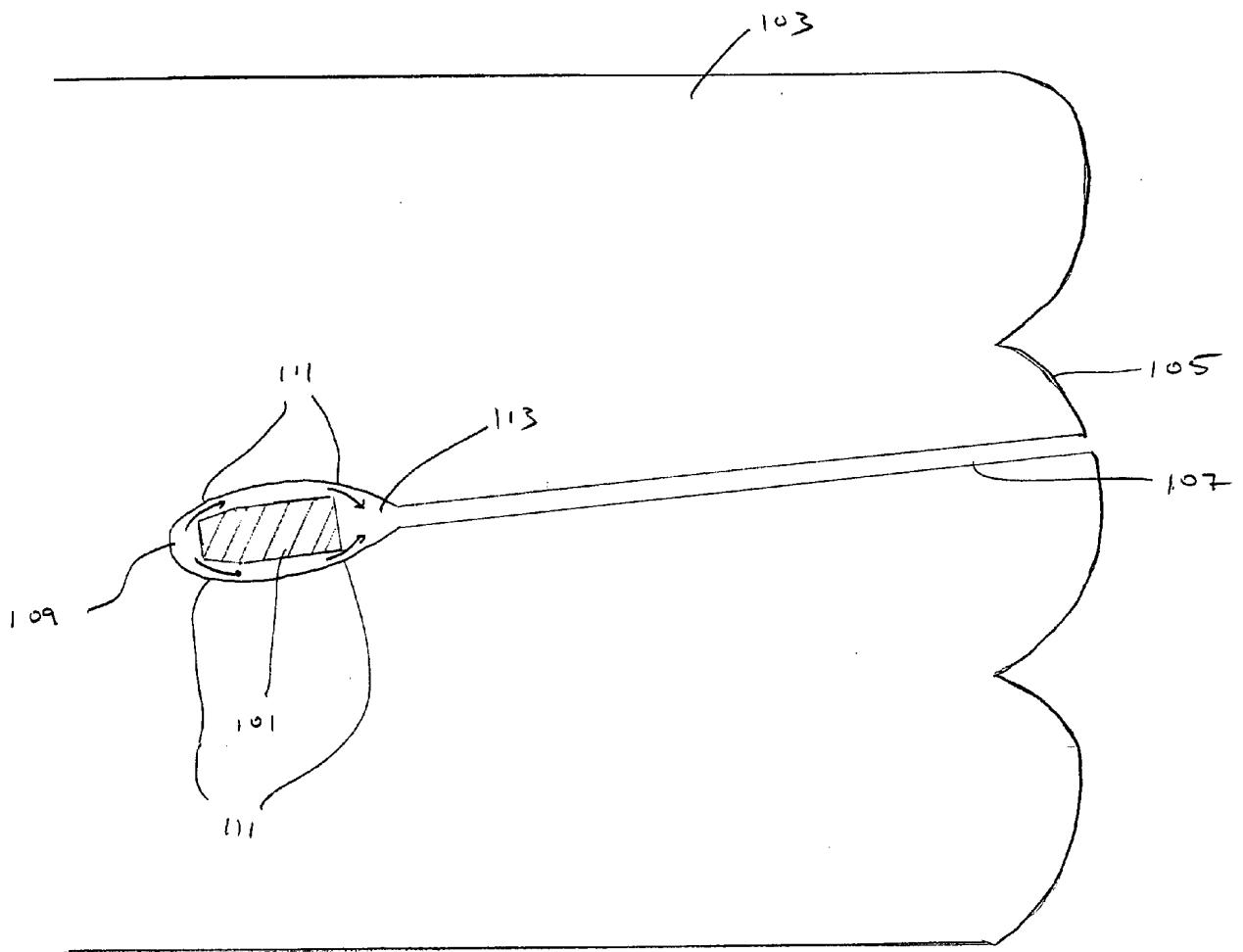


FIG. 1

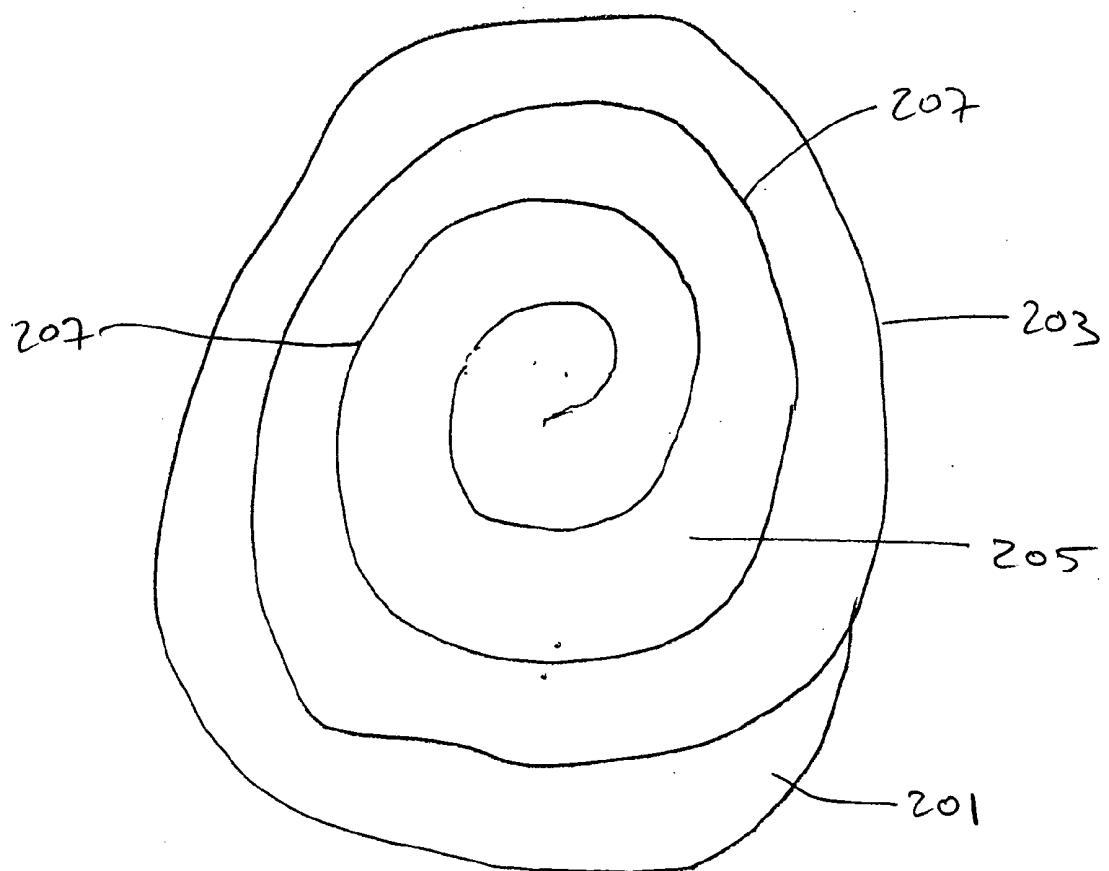


FIG 2

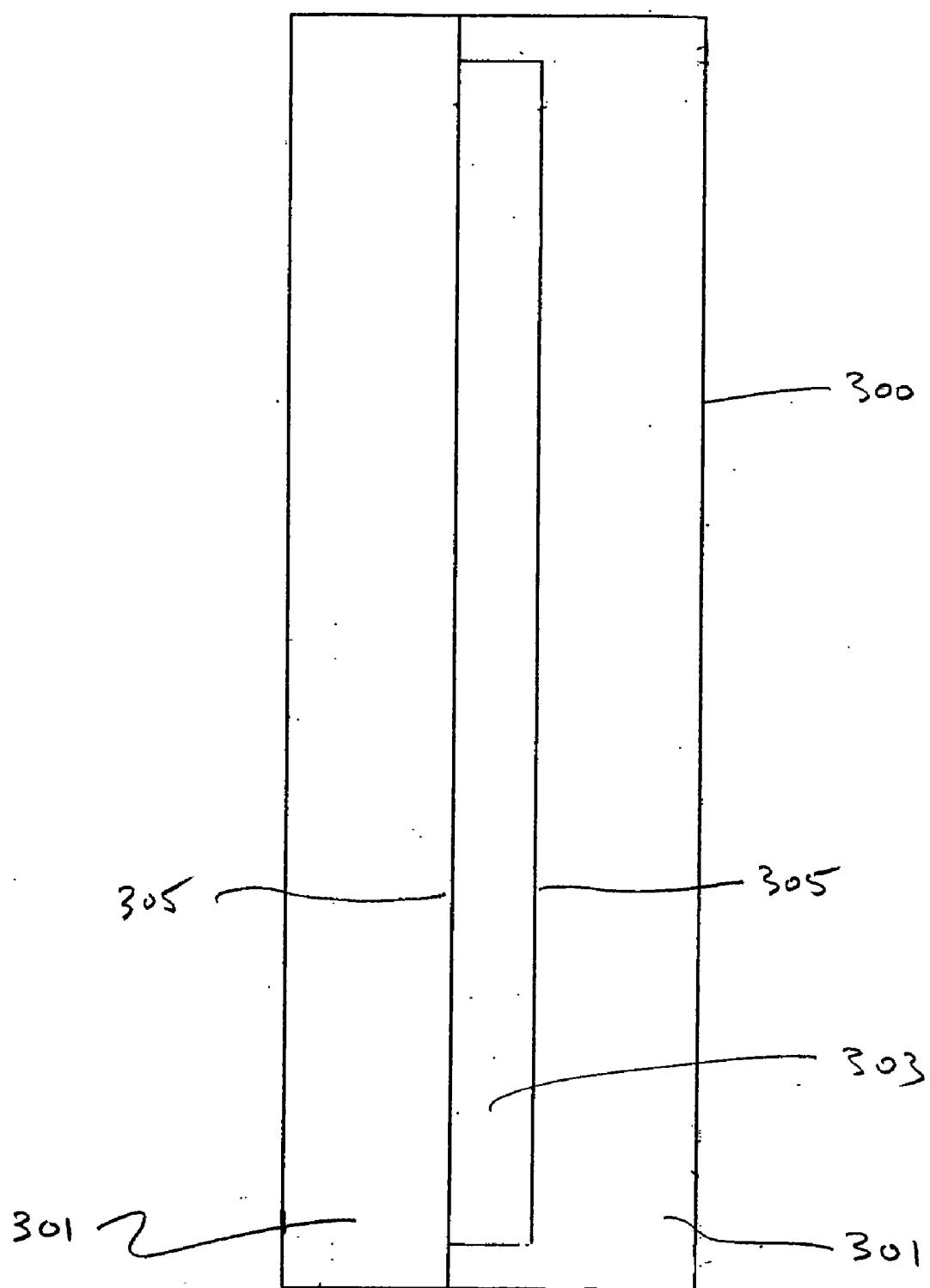


Fig. 3

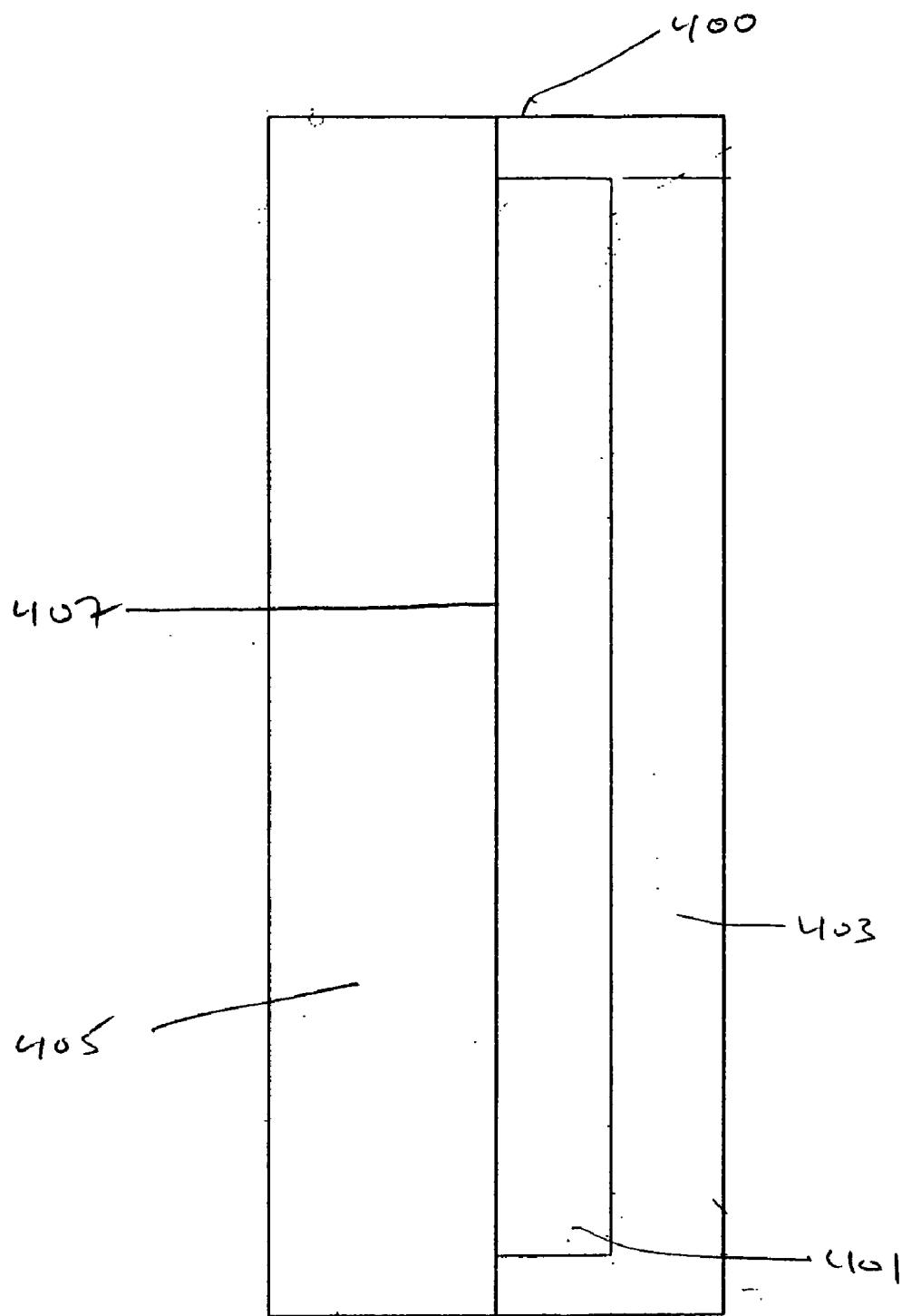


FIG. 4

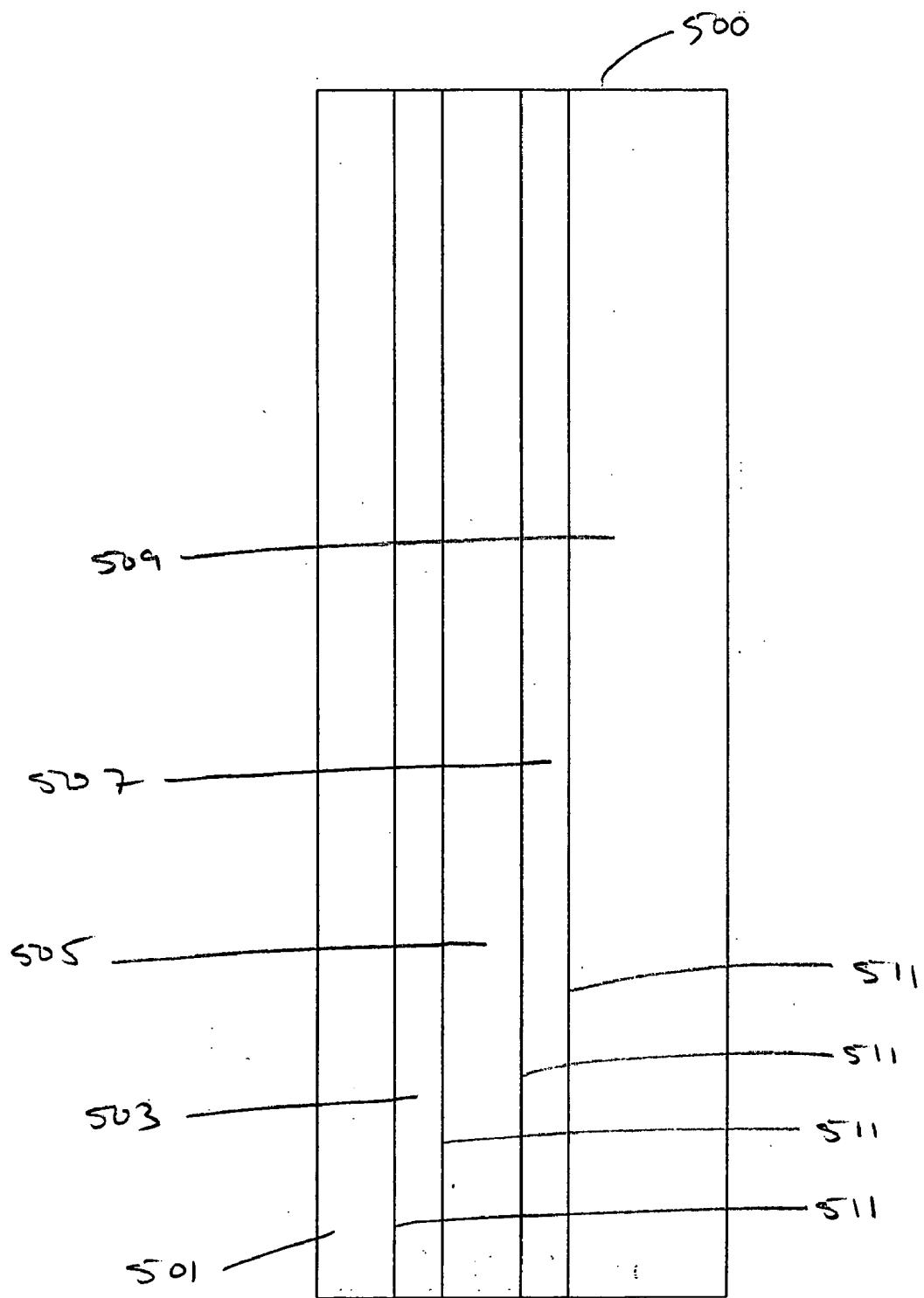


FIG. 5

## POLYMERIC BALLISTIC MATERIAL AND METHOD OF MAKING

### BACKGROUND OF THE INVENTION

#### [0001] 1. Field of the Invention

[0002] This invention relates to polymeric compositions and composite materials suitable for use in ballistic applications, and articles made from these compositions and materials, particularly articles suitable for absorbing ballistic impact. The invention also relates to methods for preparing these compositions and articles.

#### [0003] 2. Description of Related Art

[0004] Currently several types of ballistic shields are made from polyurethane polymers for transparent window shielding applications (i.e., in "bullet-proof glass"). Other ballistic materials developed in the 1970's include shields made from ceramics, and from aramid (e.g., Kevlar) fibers in various configurations. These materials have been suggested and used as lightweight armor for stopping bullets of specific design and specific velocities. Ceramic and aramid fibers have also been combined into a ballistic material. Ceramic and concrete based ballistic materials have also been used to protect personnel in armored vehicles.

[0005] The above shielding systems each have their own limitations in various aspects of design and respective physical properties. The ceramic aramid fiber composite armor is able to stop some, but not all, projectiles. Military helmets made from Kevlar or aramid fibers are best at stopping low velocity bullets or projectiles including bomb fragments, explosive debris, or deflection bullets. High velocity bullets fired from rifles are not stopped with fabric/composite systems. The subsequent result has been injurious and sometimes fatal. As a result, aramid fiber systems are considered somewhat unreliable.

[0006] Moreover, once a Kevlar or aramid fiber shield or fabric shield is compromised, e.g., by a ballistic impact, the shielding device can no longer be used, and should be discarded. The expense of replacing these armaments is extremely high, and repair is not possible. As a result, use of ballistic fiber or fabric armor in combat or training is very expensive.

[0007] Similar problems occur with ceramic armor. While some ceramic shielding is effective at stopping bullets of many sizes, powers, and/or velocities, most ceramics are quite brittle; once a round hits the ceramic shield, the shield must be replaced for fear that another encounter at a future time would provide no protection. Security of the shielded person is a constant concern, due to the fact that multiple hits may compromise the shield, and changing plates or armor may not be possible during combat.

[0008] As a result of the considerations described above, there remains a need in the art for a lightweight, inexpensive, compact, and durable protective material that will effectively absorb and disperse the energy of ballistic materials, such as bullets, slugs, sabot slugs, shrapnel, and the like.

[0009] In addition to the ballistic armors described above, other methods for stopping ballistic materials have been described. One example of such a system is described in U.S. Pat. No. 6,722,195. This system is designed for trapping and recovery of projectiles fired under highly con-

trolled conditions, so that the striations on the projectiles and other forensic indicators can be examined. The apparatus consists of an elongated trough in which are alternating layers of fibrous material and foam. A projectile fired into the apparatus first passes through a layer of fibrous material, which partially envelops the projectile, protecting its surface and increasing its cross section as it enters the next layer, which is made of foam. The increased surface area creates friction with the foam, which slows down the projectile. If the first foam layer does not stop the projectile, it will pass through another layer of fibrous material, and the process will repeat until the projectile has stopped. The trough can then be opened and the projectile removed, in essentially the condition it was in when it left the barrel of the firearm.

[0010] While this system is quite effective, it is designed to be used in obtaining projectiles for subsequent analysis under highly controlled conditions, by skilled marksmen or forensic technicians. It is not designed or suitable for stopping projectiles under the less controlled, but more realistic and common, conditions found in a firing range, backyard, or combat. Moreover, the need to recover the projectile in pristine condition so that subsequent analysis can be performed has necessitated that the system be rather elongated. Because of the length that the projectile may have to travel before stopping, the projectile should be fired along a trajectory substantially parallel to the longitudinal axis of the trough. This requirement renders the use of the device impractical in other than controlled laboratory situations. As a result, there remains a need in the art for a material that can stop ballistic projectiles that is compact, and not particularly limited with respect to the orientation of the projectile relative to the material.

[0011] Conventional ballistic traps are also bulky and heavy, due to the large amount of material necessary to effectively stop projectiles. This can create problems, e.g., where steel or other materials are used to trap projectiles. As an example, tactical police and military training involving multistory buildings is extremely difficult. Rounds fired at targets in the upper stories of these buildings must be trapped effectively because high powered projectiles fired upward may travel significant distances and injure people or property. However, conventional ballistic traps are difficult to use above ground level because of the strain their weight places on the building structure. As a result, there remains a need in the art for a material that is relatively lightweight, and that can be used in multistory tactical training.

[0012] In addition, ballistic traps used in firing ranges generally do a poor job of containing the projectiles. Since most projectiles contain a significant amount of lead, fragmentation and ricochets can result in a significant amount of lead entering the environment, particularly at firing ranges. There remains a need in the art for a ballistic trap that can retain within it the lead from projectiles fired at it, making disposal of the lead much easier.

### SUMMARY OF THE INVENTION

[0013] This invention relates to a polymeric ballistic material comprising a high molecular weight, high density polyethylene (HMW-HDPE), and to articles made from this ballistic material suitable for stopping projectiles. The articles may include backstops for firing range and home use, armor for vehicles, personnel, and aircraft, training

targets, protection for temporary or mobile military and/or police installations, buildings, bunkers, pipelines and/or any "critical need equipment that might require protection from ballistic impact, and the like.

[0014] As a projectile enters the material, its kinetic energy is converted into heat; the region in front of the projectile is compressed and melted. This molten polymer is then pumped past the projectile and forced into the region behind the projectile where it cools and hardens, with the result that the track of the projectile is of smaller diameter than the projectile itself. Moreover, because the molten region ahead of the projectile generally extends beyond the diameter of the projectile itself, the shear stress imposed by the surface of this molten polymer volume moving through the solid provides an additional sink for the kinetic energy of the projectile.

[0015] For projectiles that are spinning (e.g., projectiles fired from a rifled barrel or rifled slugs fired from a smooth bore barrel, such as a shotgun), it is believed that the energy resulting in the rotational motion of the projectile is at least partially dissipated by the shear between any projectile surface in contact with polymer, and by the pumping action that the projectile rotation exerts on the molten polymer. Rotation of the projectile effectively pumps molten polymer to the rear of the projectile, dissipating the projectile energy, and helping to slow its forward motion (in much the same way that a twist drill ceases to penetrate a wood block when it stops rotating).

[0016] Desirably, the polymeric material contains at least one density gradient at an angle to the projectile path. Without wishing to be bound by theory, it is believed that the difference in density across the projectile results in a difference in coefficient of friction across the projectile cross section. As the projectile moves through this region of differential density, the differences in coefficient of friction causes the polymer to exert different frictional forces across the projectile. The aspect ratio of the projectile with respect to its path through the material increases, drastically increasing the energy transfer between the projectile and the material. The sooner that this change in aspect ratio ("tumbling") begins to occur, the more rapidly the projectile will be stopped and captured by the material or apparatus.

[0017] In particular embodiments, the invention relates to a ballistic apparatus having at least one layer of extruded polymeric material containing HMW-HDPE. In a particular form of this embodiment, the extruded polymeric material is wound into a coil or disk. Multiple coils or discs can be bonded together, increasing the thickness of the apparatus. Moreover, in a particular embodiment, one or more coils or discs of relatively high density material can be encased within or between layers of a lower density material, forming a composite structure.

[0018] In other embodiments, the ballistic apparatus of the invention can be used as a firearm backstop, e.g., at a firing range or live-fire training facility. In another embodiment of the invention, the ballistic apparatus can be used a protective ballistic armor by disposing it adjacent to the structure to be protected. Non limiting exemplary structures include personnel, building structures, ground vehicles, aircraft, space-craft, ships, and pipelines.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0019] FIG. 1 is a schematic view of a portion of one embodiment of a ballistic apparatus according to the invention, illustrating the liquification of polymer and pumping of the liquefied polymer material in the region of the projectile path.

[0020] FIG. 2 is a schematic view of a coil or disc of polymeric material according to one embodiment of the invention.

[0021] FIG. 3 is a schematic cross sectional view of one embodiment of a ballistic apparatus of the invention.

[0022] FIG. 4 is a schematic cross sectional view of another embodiment of a ballistic apparatus of the invention having differing thickness lower density portions.

[0023] FIG. 5 is a schematic cross sectional view of another embodiment of a ballistic apparatus of the invention having a plurality of layers of different composition.

#### DETAILED DESCRIPTION OF SPECIFIC EMBODIMENTS

[0024] After an extensive investigation and testing it was discovered that a particular type of polyethylene proved a suitable shielding material for stopping and retaining high velocity projectiles, including those fired from handguns, rifles, and shotguns, as well as shrapnel. The polymer is a thermoplastic, HMW-HDPE having impact resistance and melt flow properties sufficient to absorb the energy from a wide range of projectiles, including those fired from handguns, e.g. .22, .357 magnum, .45, and .50 calibers, as well as 7 mm Tokarev and 9 mm Luger rounds. Rifle and shotgun rounds tested included those fired from an AR-15 or M-16 assault rifle (.223 caliber, 5.56 mm), an AK-47 assault rifle (7.62 mm), 12 gauge buckshot loads, 12 gauge rifled slugs, and 12 gauge sabot slugs.

[0025] The bulk polymer's resistance to impact and melt flow was sufficient to absorb the energy of all types of incoming projectiles. Desirably, the polymer is extruded or otherwise oriented in a direction substantially perpendicular to the expected trajectory of the projectile. Ballistic apparatus incorporating the polymeric material have been designed according to the invention to increase the likelihood of such an orientation, even for low angle projectiles. High velocity projectiles are stopped when they enter perpendicular to the direction of orientation of the thermoplastic polymer.

[0026] As the literature indicates, the high molecular weight polyethylene polymers have the ability to orient their polymeric chains without crystallization, due to entanglement of the polymer chains. This is not true of low molecular weight HDPE (LMW-HDPE). Low molecular weight HDPE can be drawn six to twenty times its normal elongation, while high molecular weight HDPE can draw only one to four times its normal elongation without breaking. However, low molecular weight HDPE is brittle to sudden impact. Without wishing to be bound by any theory, it is believed that when low molecular weight HDPE cools, its shorter chains experience less entanglement, allowing this form of HDPE to solidify from an essentially amorphous or liquid melt into distinct, highly packed and oriented phases. In these zones or phases, the polymer crystallizes in a manner

similar to that of a micro-crystalline wax. Because low molecular weight HDPE contains a high population of crystalline zones, it provides a more brittle matrix. This brittleness is generally not observable at room temperature under normal conditions, but can lead to stress cracking easily at low temperatures or under sudden impact.

[0027] High molecular HDPE is so entangled with long chains that crystallinity is minimized. In general, the characterization of HMW-HDPE and LMW-HDPE classifies LMW-HDPE as an HDPE with a molecular weight between about  $2.5 \times 10^5$  and about  $8.0 \times 10^5$  Daltons. HDPE's with molecular weights below these values are too crystalline and brittle for use in ballistic materials and shatter on ballistic impact. HDPE's with molecular weights in or above the  $10^6$  to  $10^7$  Dalton range are classified as HMW-HDPE. At these molecular weights, the HDPE is believed to become more amorphous in nature and its crystallinity is minimized. The resulting material is an extremely tough thermoplastic material, which can be viewed as having elastomeric properties. Exemplary suitable HMW-HDPE materials include, but are not limited to, Exxon HMW HDPE, Huntsman Chemical HMW HDPE, BP HMW HDPE, and Equistar, L4912; L5906. Other HMW-HDPE materials having properties described above are also suitable for use in this invention, including reground scrap HMW-HDPE, etc.

[0028] While both types of HDPE are formed using similar processes, chain extension in HMW-HDPE is usually achieved by chemistries involving metallocene catalysis. The crystallinity of the HMW-HDPE is minimized by a relatively high level of chain entanglement, which prevents the polymer chains from sufficiently aligning in three dimensions to form appreciable crystallinity.

[0029] Because of its different structure, HMW-HDPE exhibits different polymer dynamics than other HDPE. It does not flow very well at its intrinsic melt temperature, but instead congeals into a rubbery mass, having an elasticity similar to that of a rubber ball. It is difficult to orient at low temperatures without breaking during the draw down process. HMW-HDPE appears to have lost its crystalline properties and resembles a frozen liquid or amorphous gel, much like a vulcanized elastomer. Since crystallinity is restricted by long polymeric chains, only slight dispersions of micro-crystallites are possible. Its melt viscosity is very high; consequently the pressure to move or pump it is over 1600-2000 psi. at 450° F.

[0030] However, when super heated, HMW-HDPE will become fluid and can be made to flow to some degree. This is what occurs when a high velocity projectile strikes the polymer. When the polymer is pulled or stretched in this super heated state, it will cool quickly, and revert to its congealed state. As a result, the cooling polymer acts like an extremely aggressive adhesive with respect to anything it contacts, such as a spinning projectile. This adhesion can be promoted by using a maleated HDPE and compatible adhesion promoting agents, such as polyethylene acrylic acid.

[0031] As it cools, the polymeric material attempts to return to its original position. Ballistic apparatus made with the polymeric material were observed to prevent projectiles from penetrating more than an inch or so; some were forced back toward the surface of the apparatus and ejected from it entirely by the restoring force of the cooling polymer. When projectiles penetrated further, the initial hole of entry closes

very rapidly, trapping the bullet in the apparatus. This is especially true when the apparatus contains a layer of HMW-HDPE foam at the surface, and a higher density HMW-HDPE material near the core. Because of the energy absorbing properties of the polymeric material, the change in density along the projectile trajectory through the material, and the expansion of the polymeric material as it cools, the projectile is truly captured by the apparatus with no chance of escape, and stops within a short distance.

[0032] The behavior of the polymeric material of the invention when subjected to projectile impact is schematically illustrated in FIG. 1. Projectile 101 has penetrated polymeric material 103 by impacting curved surface 105 and traveling along path 107 into the material. A compression zone 109 approximately forward of the front end of the projectile 101 substantially liquefies the polymeric material in front of the projectile. The forward motion of the projectile, combined with any spin of the projectile about its longitudinal axis will pump the liquefied polymer along the sides of the projectile, as indicated by arrows 111, into a rear solidification zone 113, where the liquefied polymer collects and hardens, narrowing the track of the projectile to a diameter smaller than that of the projectile itself.

[0033] Table 1 below shows experimentally determined penetration depths for various caliber projectiles fired into the HMW-HDPE material of the invention.

TABLE 1

<u>Experimental Firings</u>		Penetration (in.)
<u>Hand Guns</u>		
357 Mag.		1-1.3
.22 Cal.		0-.25
.45 Cal.		.25-.50
9 mm		.75-1.25
<u>Rifles (High Powered)</u>		
AK-47		5.75-11.00
M16		5.00-8.00

[0034] The change in density along the projectile trajectory provides an important and advantageous feature to the apparatus of the invention. The change in density causes a change in aspect ratio (or tumbling), which rapidly increases the energy dissipation of the projectile; the sooner the projectile tumbles, the shorter the distance required to capture it.

[0035] As part of the invention, it has been discovered and observed that as the degree of orientation of the polymer strands in the material is increased, the curvature of the trajectory of the projectile in the polymer increases as well. Without wishing to be bound by theory, it is believed that this effect results in part because the spin of the bullet biased its forward direction to a certain degree as it encountered each fiber. Hence, as the bullet encounters more fibers, it turns, changing its aspect ratio relative to the orientation of the fibers, until eventually it either stops or begins to tumble.

[0036] It has also been discovered that if the density of the polymer changes significantly, then the bullet changes direction and travels toward a lower density zone. When this

occurs, the bullet begins to tumble. When the bullet left a higher density zone and entered a lower density zone, the bullet became unstable resulting in tumbling or curved trajectory. In all events the polymer absorbed the kinetic energy of the projectile and converted it into heat that was observed as melted polymer and/or a general warming of the polymer mass.

[0037] It was also observed that low velocity projectiles (and in particular, low angle low velocity bullets) bounce or ricochet off of the material if the surface density was too high, e.g., around 0.95 to 1.5 g/cc or higher. Accordingly, it is generally desirable to use a material having a density at the surface of between about 0.2 g/cc and about 1.5 g/cc (for a filled material). Densities that are lower (below about 0.2 g/cc), while still usable, increase the risk that high powered projectiles can penetrate through the material, and are therefore not recommended unless the material will only be subjected to low velocity projectiles, and unless the material is particularly thick (e.g., has a thickness ranging from around 6 to around 20 inches, which may not be cost effective or efficient).

[0038] This density can be controlled at the time of manufacturing by incorporating exothermic blowing agents, endothermic blowing agents, or a mixture of these. The concentration of blowing agent necessary will depend somewhat on the temperature and pressure of the extruder. For example, incorporation of about 0.5 pph FOAMAZOL 50 or FOAMAZOL 81 (Bergen Intl.) blowing agent into an extruder running at blowing set temperature of about 400° F. will provide an open cell foam having a density of about 0.86 g/cc; operating the same extruder at a temperature of about 385° F. provides a closed cell foam having a density of about 0.6 g/cc. Other suitable blowing agents include calcium hydroxide, and citric acid—sodium bicarbonate (HYDROSEROL). Density can also be controlled by addition of filler materials. These can be fibers or particulates that are wetted for incorporation into the polymeric material (e.g., fillers treated with wetting agents such as Amplify 204 (Dow Chemical), or silane- or titanate-treated fillers) can be coupled efficiently to the polymeric material. These fillers also provide a more uniform melt viscosity.

[0039] For higher velocity projectiles, higher densities are required to slow down and stop the projectile. However, high velocity projectiles striking a high density surface can deflect or ricochet, as described above. Several features of certain embodiments of the ballistic material of the invention help to avoid this occurrence. First, orientation of the projectile trajectory to the material surface is desirably at a relatively high angle (perpendicular, if possible). This helps to increase the likelihood of capture of the projectile by the material, and begins the process of changing the projectile aspect ratio very quickly. Since projectiles are likely to contact the material from a variety of angles relative to the overall plane of the material, certain embodiments of the invention include a material surface that is not flat, but is wavy and varying, as shown by surface 105 in FIG. 1. One method for achieving this profile is to extrude the polymeric material in the form of a tube 201, and wind the tube into a spiral plate 203 whose faces 205 form the surfaces that contact the projectile, as illustrated schematically in FIG. 2. The surfaces of tube 201 come into contact as the spiral is wound, forming higher density regions 207. The repeated curvature of the surface of the face of the material increase

the likelihood that even a projectile traveling at a low angle with respect to the plane of the material will contact the surface at a high angle, increasing the likelihood of capture, and decreasing the likelihood of ricochet.

[0040] In addition to the repeated curved surface, capture of the projectile can be enhanced by providing a comparatively low density jacket or shell around a comparatively high density core. A cross sectional schematic of one embodiment of such an apparatus 300 is shown in FIG. 3. The lower density jacket 301 may be the same polymeric composition as the higher density core area or "hard plate" 303, but more highly foamed. Alternatively, two different polymeric formulations of different density may be joined together, with the lower density polymer disposed toward the projectile trajectory. The outer layer of less dense polymer 301 ensures that the projectile is trapped, while the density change from the outer material to the inner material significantly changes the projectile's aspect ratio with respect to the oriented polymer.

[0041] Moreover, the interface 305 between the high density and low density material can act as an accumulation zone for projectiles absorbed by the apparatus. Either or both layers may contain additional density gradients within them that help to change the aspect ratio of the projectile and trigger tumbling. Tumbling causes the projectile to transfer energy much more efficiently to the polymer mass, resulting in a more rapidly captured projectile. Whether bullets are high or low velocity, deformation occurs to the bullet with full metal jackets, while All bullets made entirely of lead (unjacketed) were deformed or totally destroyed.

[0042] The hard plate/foamed jacket construction provides excellent density gradient for initiating tumbling of the projectile, and can be constructed to provide an accumulation zone for projectile material as described above. The hard plate as described above can be high density HMW HDPE with a typical density of 0.86 g/cc to 0.965 g/cc (with no fillers). The inclusion of fillers can increase the density of the hard plate to 1.4 g/cc or more. However the hard plate can also be a ceramic or metal material in order to obtain even higher densities, if desired for particular uses. The configuration of the hard plate can be varied by installing a steel ballistic plate or block of steel within the apparatus having a particular desired shape or orientation. The hard plate can also be perforated, even to the point of using a heavy duty mesh that can be set in the mold to be surrounded by HMW HDPE and/or other composite material. These heavily reinforced apparatus can be used in fortifications in walls, large shields for armored vehicles, bulkheads, pipelines, pump stations, and the like to protect them from attack by explosive devices, gunfire, artillery, etc.

[0043] The embodiment shown in FIG. 3 is reversible as illustrated, as both layers of foam are shown to have the same thickness. However, it is also possible to make a ballistic apparatus that is not reversible, but that has a thicker lower density layer on one side, in order to provide even more effective capture of projectiles. Such a ballistic apparatus 400 is illustrated schematically in cross section in FIG. 4. In this embodiment, the higher density plate 401 is disposed between a relatively thin lower density layer 403, which serves as the back of the apparatus, and a relatively thick lower density layer 405, which serves as the front of the apparatus. This relatively thick front layer 405 provides

for increased capture and retention of the projectiles fired into it due to the increased flowability and pumping of polymer along the path of the projectile, but still provides very effective stopping power due to the density gradient between the outer layer and the higher density core. Moreover, interface 407 provides an effective tumbling zone for accumulation of projectile material during use.

[0044] In addition to HMW-HDPE, the polymeric material can contain a number of other components to provide the ballistic apparatus of the invention with desirable properties, including orienting the polymer chains during extrusion, entangling the polymer chains, and providing density gradients within the polymeric material to induce early tumbling or aspect ratio change. Typical compositions include (percentages are by weight based on the total weight of polymeric material):

[0045] HMW-HDPE in amounts ranging from about 40% to about 100%;

[0046] Maleated HDPE and/or acrylic acid (for adhesion control, in amounts ranging from about 0.25 to about 10%);

[0047] Macro and micro fibers, such as silica, alumina, or organic fibers, in amounts ranging from 0 to about 50%, more particularly from about 5 to about 10%;

[0048] Peroxide-containing or silane-containing curing agents, in amounts ranging from 0 to about 4%; the material can contain at least two different types of silanes simultaneously, which may each perform independent functions: (1) a curing silane, typically a vinyl silane used with peroxide and catalyst; and (2) a treatment silane, typically of the amino or epoxy types for pigment treatment, to control coupling and melt rheology.

[0049] Colorants, in amounts ranging from 0 to about 12%;

[0050] Plastomer (for control of crystallinity and curing) in amounts ranging from 0 to about 20% (e.g., ENGAGE 8540 (Dupont Dow); EXXACT 2030 (Exxon), etc.);

[0051] Vistalon rubber (for control of crystallinity and to provide entanglement at low temperatures) in amounts ranging from 0 to about 30%;

[0052] Natural rubber (desirably in crumb form, to provide elasticity and as a filler) in amounts ranging from 0 to about 25%;

[0053] EPDM rubber (desirably in crumb form, to provide low temperature entanglement) in amounts ranging from 0 to about 50%;

[0054] Grafting/crosslinking catalyst(s) (such as catalyst T-12, Air Products, Inc.) in amounts ranging from 0 to about 0.5%;

[0055] Lubricant (such as a wax or metal stearate, such as zinc stearate) in amounts ranging from 0 to about 12%;

[0056] Wetting agent (such as stearic acid) in amounts ranging from 0 to about 4%;

[0057] Fillers (such as ceramic (e.g., silica, alumina, and/or zirconia) plates, powders (particularly those having high aspect ratios), and/or spheres) in amounts ranging from 0 to about 30%;

[0058] Vulcanization agents (such as sulfur-containing crosslinking compounds) in amounts ranging from 0 to about 8%. It is understood that, when vulcanizing agents are used, zinc oxide and zinc containing derivatives can be included to accelerate the reaction, and magnesium oxide (such as Mag-lite "D" from Merck) can be used to modify and stabilize the vulcanization mechanisms. Additional components can include fire retardants, such as magnesium hydroxide, boric acid, zinc borate, aluminum trihydrate, and various clays including but not limited to montmorillonite, talc, bentonite, and kaolin (nano-clays).

[0059] It will be understood that a range of amounts including 0% indicates that the component is optional, and its presence is not necessary to fall within the scope of the invention. It is also understood that various components, such as UV absorption packages (UV absorbers, UV stabilizers, antioxidants, and the like) can be included in the HMW-HDPE as obtained, or may be added separately. Further, blowing agents can be included in amounts appropriate to regulate the density of the polymeric material to desired levels.

[0060] Inclusion of rubbers (such as Vistalon, natural rubber, CPE (Chlorinated polyethylene), TPO (thermoplastic polyolefins), TPV (thermoplastic polyolefin vulcanite), or EPDM rubbers) is desirable to provide desirable energy absorption properties at low temperature uses (e.g., in arctic or Antarctic environments). Inclusion of fibers and ceramic fillers helps to provide density changes and initiate tumbling in high temperature uses (e.g., in desert or tropical environments). Inclusion of both types of additives can provide a material suitable for use in a wide range of environments.

[0061] The inclusion of maleated HDPE in the composition provides additional adhesion, both to the projectile entering the ballistic apparatus, and of the polymeric material to itself, allowing the extruded polymeric material to be, in effect, hot melt adhered to itself. This allows the material to be formed into a variety of shapes, such as coils or zig-zag shaped plates, wherein the outer surfaces of the extruded tubes of polymeric material will adhere together. This feature also allows for plates of the material to be adhered together by placing them into contact while hot or during heating. The higher density outer skins of the extruded polymer tubes adhere together, creating a thicker higher density region, surrounded by two lower density regions. As the projectile passes through these density gradients, its aspect ratio begins to change.

[0062] Various fibers can be added to the material to increase the orientation of the polymer in the flow direction. Fibers were added to the polymer utilizing high speed mixing and/or by an additive feeder so as to control the dispersion of the fiber in the polymer. The fibers used can include one or more of the following: nylon, long and short; carbon, long and short; ceramic (alumina), (silica), (zirconia) and long and short; aramid (chopped, pulped), cellulose-from Kenaf, cotton, wood pulp and wood flour; ground carpet fibers; polyester-fabric; and metal fibers.

[0063] These fibers can be added in differing amounts in different layers of the ballistic apparatus 500 of the invention, as illustrated schematically in FIG. 5. In this embodiment, a first higher density layer 501 is disposed adjacent to a first lower density layer 503, which is in turn disposed adjacent to a second higher density layer 505, which is

disposed adjacent to a second lower density layer 507, which is in turn disposed adjacent to a third higher density layer 509. This alternating structure of higher and lower density layers provides several tumbling zone interfaces 511, whose density gradients help promote tumbling, and whose interfaces can expand to accumulate projectile material. The density variations between higher density and lower density layers can be achieved by filling the polymeric material with, e.g., fume silica in the higher density layers, and using unfilled polymeric material in the lower density layers. The higher density layers may be varied in density from each other by including differing amounts of filler. A particularly desirable arrangement is to have the successive higher density layers increase in density along the projected path of the projectile (e.g., layer 509 has a higher density (and higher filler content) than layer 505, which in turn has a higher density than layer 501).

[0064] In addition to modifying the composition of the polymeric material, orientation and density gradients can also be affected by the production process itself.

[0065] The polymeric material of the invention can be oriented by drawing or extrusion, followed by quench cooling and extending or stretching (which can occur nearly simultaneously). This will generally provide good extension and orientation of the polymer chains without breakage, but with some resistance to the orientation process.

[0066] Extrusion parameters, such as the extrusion die or nozzle size and shape, can be varied to optimize results. For example, nozzle size can be varied from around 1.5 inches down to around 0.0625 inch, to more completely force orientation in the extruded flow direction. It has been found that the smaller the diameter of the nozzle, the higher the melt or extrusion temperature has to be in order for the HMW-HDPE to flow as desired. The shape of the nozzle cross section can be varied from circular, to square, to diamond, to oval, to star-shaped, to cross-shaped. For air or polymer injection, various mandrels were developed to be used with the nozzle to complement co-extrusion techniques used in the manufacturing of the final molded product. Examples include tubular mandrels for air injection.

[0067] Process parameters relating to cross-linked the HMW-HDPE with small quantities of peroxide and/or silane with tin catalyst increase the molecular weight of the polymeric material by tying up gel polymer, increasing entanglement to flow, and enhancing the bullet capturing ability of the material. The primary objective of modifying these processing parameters is to provide a material that can capture and retain a projectile within the polymer mass within a thickness of two inches or less for low velocity projectiles, and in less than 6 inches for high velocity projectiles, such as bullets from high-powered rifles.

[0068] Process parameters directed to controlling density so as to retain the projectile and initiate tumbling or change in aspect ratio include:

[0069] a. Controlling pressure in the mold by pressurizing a preheated mold and maintaining it for extended period of time without the pressure destroying the mold. This necessitated pre-design of molds to withstand this extended heating.

[0070] b. Introducing gas into the polymer in order to create low-density masses of polymeric material; gas introduction can be accomplished by several methods:

[0071] (1) including a blowing agent such as an azo type-blowing agent (e.g., Celogen, Uniroyal), bicarbonate, or other exothermic or endothermic blowing agents. While both types work well, the azo-type blowing agents continue to provide gas injection after the mold had set. This can be dangerous to the mold if the azo adjustments are not balanced properly.

[0072] (2) injecting air or other inert gas into a nozzle via a mandrel while the mold is being filled. The mandrel can be made of various shapes, as described earlier. This method has the advantage of adding air when desired, so that density is controlled and varied in specific locations of the polymer mass. Air bubble size is controlled by breaker plate design and/or static mix head for this method.

[0073] c. Incorporation of other polymers to increase capturing ability of the polymer as well as controlling density. The polymers can be introduced in a melted state in a similar manner to that used to inject air through the nozzle; however, the polymer injection was done with the use of an auxiliary extruder. Suitable polymers include: polyethylenes having different grades and densities (particularly useful are the current plastomers of PE, such as TPO's, and TPV'S), EPDM, various rubbers, urethane-TPU, urethane, polystyrene, block copolymer of SBS, SEPS, and PP, alpha polyolefins, rubbery epoxies and combinations of these. If fibers are to be added as described above, they may be introduced by being incorporation into any one of the polymers listed to increase bullet capturing ability. Particularly suitable are the urethanes, (one component and two components), typically used for bulletproof windows. These urethanes TPM can be introduced by low pressure in a manner similar to the air injection technique described above, either through a nozzle or injection molding equipment.

[0074] d. Fibers can be added in a uniform manner with the controlled dispersion method so that fiber was added to specific regions of the apparatus, depending upon its design. For example, the fiber can be placed in the polymer mass in particular locations to further improve the efficiency of bullet capturing in those regions. The fiber addition was added through the auxiliary extruder via a mandrel in the nozzle where the air was introduced. By dispersing and injecting fiber into polymer and disposing this polymer in certain areas of the ballistic apparatus, the degree of ballistic protection can be increased, even though the ballistic apparatus itself is relatively small or thin. Fiber introduction did not catch on the breaker plates during extrusion, so fiber of various types can be used in chopped or pulped compositions. In order for fibers to be effective in the design they should be matted in the interior zones of the ballistic apparatus. The ballistic material of the invention can be made by several techniques, two of which are described below. It will be understood that other, similar techniques can be used to prepare the ballistic material of the invention, such as manipulating the extruded material by hand, etc., and that these are intended to included within the scope of the invention.

#### I. Injection Molding System:

[0075] A mold is designed for the desired shape and configuration. The mold is then injected with polymer at controlled temperature and pressure by delivering the polymer through a standard nozzle or a complex nozzle. The

complex nozzle is designed to receive another polymer from an auxiliary extruder to give a co-extrusion extrudate. It is equipped with a mandrel to control the shape and speed of delivery of the co-extruded extrudate. Both extruders are desirably synchronized, so that each extrudate is matched in speed and temperature. Once the mold is filled, the polymer in the mold is pressurized so that the mold is completely filled and the deformation on cooling is minimized. The mold design is fabricated from aluminum or steel, with steel being the preferred material for a clamshell design. Heaters can be installed in the appropriate positions on the mold, and help to promote complete filling of the mold, so that the formation of void spaces is minimized.

[0076] Vents may also be installed to permit rapid filling of the mold. The input nozzle is equipped with a pressure-temperature transducer to give the final injection pressure received by the die. The die can desirably be connected by quick disconnect clamps for ease of joining the mold with the extruder and the eventual disconnection of the mold, which is best described as a clamshell mold with clamps.

## II Spindle Molding Method:

[0077] This provides one method for extruding the polymeric material of the invention into a spiral plate. In this method the polymer is extruded from the nozzle on to a spool where it is wrapped around a spool until it reaches the desired diameter. The spindle is designed with two metal discs with an axle to wrap the extruded prepared polymer. The spindle is powered by a SCR drive controller with torque and speed variable settings. The spindle is equipped with a reel that permits the extrudate to run back and forth on a winding mechanism. The winding mechanism has an eye that spins the extrudate as it passes through it and the reel on its way to the spindle.

[0078] Once the spindle is filled with extrudate to the desired level, the spindle is removed from the frame along with the reeling and spinning mechanisms. A steel band can be placed onto the surface of the polymer and wrapped around the outside of the spindle where the polymer is contained by the two discs. The discs act as guides as the polymer is confined in this containment and the heated band completes the final formation of this molding technique. The band is applied and clipped, forcing the polymer to conform to the circular band with this clamp. The result is a solid disc of polymer matrix in the shape of a large disc. The size (thickness and diameter) of the discs may vary; sizes of 30 inches in diameter and 4 to 6 inches thick have been found to be suitable as ballistic apparatus usable as backstop or on firing ranges. The method is suitable for preparation of a wide variety of disc sizes, including very small discs, weighing one pound or less.

[0079] Another technique used in manufacturing ballistic apparatus of the invention is to prepare a disc using the spindle method described above, and placing the disc in an injection mold, also described above, and injecting material around the disc. This provides the resulting ballistic apparatus with desirable properties. These enhanced dynamic properties for in-coming projectiles due to the dramatic changes in densities the projectile encounters as it moves from the molded exterior portion to the central disc.

[0080] The spiral method described above allows the preparation of multiple laminations of Kevlar or fabric

matted composites. The spiraling process allows the incorporation of single or multiple layers of ballistic fabric and/or allows the space between each layer to be filled with the polymer or polymer matrix or foamed polymer, forming a laminate. The laminate can be pressed together to fuse or partially fuse the layers thereof, and can be shaped by a mold or by hand, or in other ways to give a laminate composite with desired shapes or thicknesses, depending on the ballistic requirement. The multiple-laminate method may be done on a horizontal turntable as compared to the reel and spool method described above. The turntable gives the operator more control and increases ease of manufacturing. The center of the spiral can be made without a hollow center core. Finally, the apparatus can be compressed by hydraulic ram to hold it in place in an open mold whether round or square. This containment method shapes the apparatus into a very consistent form. The result is a shape that is reproducible each time the apparatus is made.

[0081] In the spiral methods described above, the spiral is tensioned, wrapped and the extrudate from the extruder spun to the desired degree for maximum orientation. The turntable permits ceramic plates, and/or ceramic or metal spheres to be placed in the laminate with the same ease as the placement of fabric or mesh. The objects can all be placed in the spiral matrix to facilitate impediment of any projectiles. The purpose is to force the projectile to tumble, deflect, shatter, mash, or disintegrate in the polymer matrix of ceramic objects, foam or matting. Further, the polymer absorbs energy from whatever the occurring event happens to be. In the case of the ceramic materials, multiple layers can be installed in each layer resulting in a composite that has fabric, polymer or ceramic in combinations that are strictly used to capture the projectile and its respective energy.

[0082] Multiple layered laminates of ballistic fabric or mesh are capable of impeding high velocity, high power and high spinning projectiles. The shields will become thinner as composites are developed utilizing higher density in combination with fabric and the high degrees of spiral orientation. The addition of ceramic spheres and/or metal spheres and/or ceramic plates, and/or metal plates or structural fabrications of the same only increases the energy capturing ability. In short, the ceramic or metal structures neutralize higher impulse projectiles with high power, and high spinning masses. The science of capture indicates that high density and the compression ability of the polymer results in a projectile capturing mechanism.

[0083] Additional safety features are achieved in a particular embodiment by incorporating foamed polymer in the front, back, and/or sides of the shield having a controlled density so as to prevent bouncing/ricocheting, and/or to control deflection of incoming projectiles. Both flat nosed or blunt projectiles, as well as low velocity projectiles, will deflect off of the surface. Deflections are more likely to occur if the incoming projectile is at a low angle to the material surface. Surface materials having densities ranging from about 0.965 to about 0.40 grams/cc provide and/or allow capture of most incoming projectiles, including most low angle, flat-nosed, and low velocity projectiles, because the projectiles are easily able to penetrate the lower density foamed polymeric material, pump molten polymer behind them into their path, and creating an opening smaller than the projectile's aspect ratio. The low density polymeric

material thus limits or prevents backward movement of the projectile after contacting, e.g., a more dense portion of the apparatus. This allows the projectile to be captured, so that they cannot bounce back out of the apparatus.

[0084] As described above, the density of the polymeric material can be controlled by several methods. In producing lower density foamed polymeric material for a surface layer, density may be controlled by adding a low-density polymer to the HMW-HDPE composition to lower the overall density into the desired range. Alternatively or additionally, very precise additions of closed cell blowing agents can be incorporated in the polymer matrix to lower the density to the desired values. These methods provide reproducible densities during production of the material and apparatus. The layer of this controlled/lower density polymer will typically have a thickness of between about 0.25 and 6 inches, depending on the designed purpose of the apparatus. Thicker layers will typically be used on apparatus intended to capture higher velocity projectiles, or projectiles likely to impact at very low angles. Thinner layers may be suitable for use in apparatus intended to capture lower velocity projectiles, such as handgun rounds, etc. Because the controlled/lower density polymeric material is a closed cell foam, there are few or no voids in the matrix.

[0085] By using a lower density layer in conjunction with a higher density polymeric material, the resulting apparatus provides for multiple density differentials (both between the surface and inner portion of the polymeric material, and between the higher density and lower density materials) that cause projectiles to "tumble" (i.e., to change their aspect ratio sufficiently that a substantial portion of their kinetic energy is captured by the apparatus, along with the projectile. The lower density polymeric material acts as a sort of "ricochet net". If not melted to the surface of an inner, higher density polymeric material, the gap between the layers can allow a place for the projectile material to accumulate. Because the accumulation of projectile material spreads out in the gap between polymeric material layers, it provides a further barrier to penetration by additional incoming projectiles. The apparatus is thus not compromised by the impact of additional in-bound rounds, so it is virtually impossible to "shoot through" the apparatus. In addition, the retention of projectile material, often mostly or almost entirely lead, prevents or limits the release of particles of projectile material into the environment.

[0086] The ballistic apparatus of the invention can be formed from unbonded layers of spiraled extruded polymeric material to capture and accumulate projectiles when the entire shield is composed of high density composite. The unbonded layers allow formation of "tumble zones" that slow and stop projectiles after tumbling, and provide a place for projectile material to accumulate. Ballistic apparatus designed in this way is particularly suitable for high velocity projectiles and/or projectiles exhibiting a high rate of spin, such as rifle rounds.

[0087] Additional closed cell foam methods have been developed to extrude tubules having a hollow inner area that can be filled with air or high density polymers. Incorporating air provides a foam that is not active after air is entrapped and is independent of temperature. The cells are clean, since they contain only air at atmospheric pressure.

[0088] This method also allows densities greater than the base polymer, HMW-HDPE. When the tube is filled with urethane, as an example, its density is greater than 9.965 g/cc.

[0089] The polymeric material used to make the ballistic apparatus of the invention may be filled with ceramic materials as described above. As used herein, the term "ceramic" can include, but is not limited to, materials made from zirconia, alumina, borates, and/or silica. The ceramics may be sintered (e.g., fired in a kiln to develop their grain size) or unsintered. They may be shaped into desired forms, e.g., spheres, plates and/or very fine to coarse beads. Examples of silicas include glass, novaculite, quartz, sand, each having various particle sizes, and combinations of these. Ceramics made from cements of silica, Portland cement, alumina cements, magnesium oxide cements, phosphorite cements, and/or hydrocements are especially good and very economical. They have compression values of 15,000 to 60,000 psi without sintering in a kiln. These ceramic cements can be combined with the polymeric material of the invention and can then be shaped from a liquid and poured into a void, which forms a mold for the apparatus of the invention. They may be pre-formed into plates, spheres or any other desired shape with the resulting material having the approximate hardness of sintered ceramic. Polymer ceramic cement versions used are so flexible they can stop projectiles without shattering completely.

[0090] The inclusion of ceramic elements in the polymeric material according to the invention enhances the utility of the resulting ballistic material as armor, in part because of the ability of the polymer to disperse energy prior to and after impact of the projectile with the ceramic element, thereby making the entire composite more efficient. Polymer cements (e.g., those including polymethylmethacrylate, polyacrylates, polystyrene and copolymers thereof (such as polybutylacrylate, poly-2-ethylhexylacrylate, copolymers such as polystyrenemethylmethacrylate, SBR rubber), and the like) can also be used in the invention.

#### METHODS OF USING THE POLYMERIC MATERIAL OF THE INVENTION

[0091] The energy absorbing polymeric material of the invention, and apparatus made from it, can be used in a number of applications. These include:

[0092] 1. Ballistic shields (e.g., hand held) for military and law enforcement use.

[0093] 2. Ballistic armor for military vehicles, particularly for protecting tracks, radiators, engines, personnel and other vulnerable areas

[0094] 3. Ballistic armor components for aircraft, particularly for protecting pilot compartments, avionics packages, hydraulic systems, ejection systems, fuel systems, engine housings, etc.

[0095] 4. Bullet capturing targets for sport and training, either as individual targets or complete walls; particularly suitable for tactical training targets for military and law enforcement use.

[0096] 5. Ballistic armor for mobile support facilities, such as mobile military command and control posts, communications installations, surgical hospitals, evac stations, etc.

- [0097] 6. Dock bumpers for trucks and large ships.
- [0098] 7. Shock absorber in pads for building columns.
- [0099] 8. Shields or plates forming part of tactical law enforcement or military body armor, particularly with embedded ceramic, Kevlar or nylon mailing.
- [0100] 9. Armored doors, panels etc. for armored trucks, bank vaults and other secure locations.
- [0101] 10. Protective pads for all sports activities in foam and high density layers to make composites that have multiple low and high density laminates.
- [0102] 11. Containment devices for bombs, unexploded ordinance, improvised explosive devices (I.E.D.).
- [0103] 12. Other applications where energy and impact absorption, light weight, compact size, and/or reuse are important.
- [0104] 13. Apparatus can be used for the protection of spacecraft and space personnel from flying shrapnel and solid particles since apparatus is fully vulcanized.
- [0105] The invention can be more clearly understood by reference to the following examples, which are not intended to be limiting of the appended claims.

#### EXAMPLE 1

[0106] 60 lb of HMW-HDPE (obtained as a reground HMW-HDPE waste stream containing EVOH (ethylene vinyl alcohol polymer) were combined with 0.6 lb of AMPLIFY 204 (Dow) and 0.3 lb of B.A. CELOGEN (50%) (Uniroyal) and mixed in a high intensity mixer and in an extruder at a temperature of about 400 to 450° F. The composition was extruded through a round, 1 inch diameter conical nozzle to form a tube approximately 1.5-2 inches in diameter. This tube was formed into a flattened spiral by coiling in a heated mold plate. The extruded material had a density of approximately 0.96 g/cm<sup>3</sup>.

#### EXAMPLE 2

[0107] A handgun/shotgun target apparatus was prepared by allowing the double thickness spiral material obtained in Example 2 to cool. The identical composition was prepared, except that 0.75 wt % of azo blowing agent (Bergen Intl.) FOAMAZOL 50 or FOAMAZOL 81 was added; the composition was introduced into the extruder described in Example 1, and a 4 inch thick spiral layer of material having density of about 0.37 g/cm<sup>3</sup> was extruded onto a heated mold plate. The cooled double thickness spiral was disposed onto this layer while the layer was still hot, and additional polymeric material was extruded around the edge of the double thickness material. Finally, another 4 inch thick spiral layer was extruded on top of the double thickness layer. The resulting material was removed from the mold plate and allowed to cool, forming a composite structure containing a central hard plate of higher density, and a surrounding foam layer of lower density.

#### EXAMPLE 3

[0108] A rifle target was prepared by repeating the process of Example 1, with the modification that another polymeric material containing fumed silica was included in the apparatus. The target was formed by cold laminating: a first layer

having a thickness of 2 inches and having a silica content of 16.66 wt % and a density of 1.17 g/cm<sup>3</sup>; a second layer having a thickness of 1.25 inches, a density of 0.870 g/cm<sup>3</sup> and without fumed silica, a third layer having a thickness of 2 inches and a silica content of 23.78 wt % and a density of 1.26 g/cm<sup>3</sup>, a fourth layer having a thickness of 1.25 inches, a density of 0.870 g/cm<sup>3</sup>, and without silica, and a fifth layer having a thickness of 4 inches, a silica content of 42.85 wt %, and a density of 1.499 g/cm<sup>3</sup>.

#### EXAMPLE 4

[0109] A ballistic apparatus made by the process described in Example 2 was subjected to intensive ballistic testing by firing over 7000 rounds of various calibers into it. This testing included firing 800 Makarov rounds, 2000.40 cal. rounds, 250.357 cal. rounds, 2500 9 mm rounds, 25 .50 cal. Rounds, 300 Tokarev rounds, 75 .25 cal. rounds, 100 12 gauge rifled slugs, 100 rounds of 00 gauge buckshot, 25 12 gauge sabot slugs, and 900 .45 cal. rounds, from a distance of about 3 ft, without any penetration through the target. The 100 12 gauge rifled slugs were fired into an area approximately 10 cm in diameter without failure of the ballistic material (i.e., all rounds were trapped and retained within the apparatus.

#### EXAMPLE 5

[0110] A ballistic apparatus made by the process described in Example 3 was subjected to ballistic testing by firing over 7000 rounds into the target, including 1800 rounds of AR-15 .223 cal., 2000 rounds of AR-15 .223 SS109, 3000 rounds of AK-47 7.62 mm, 180 rounds of .306 cal. FMJ, 25 rounds of 7 mm Magnum, and 60 rounds of .308 Power Point from a distance of approximately 3 ft. No penetration through the target was observed.

[0111] The ballistic apparatus prepared and tested above demonstrate the significant advantages of the invention. As rounds are fired into a conventional ballistic material, repeated projectile strikes in the same general area often results in failure of the material. In fact, for ceramic armor, a single projectile strike will render the struck armor plate useless, and require it to be replaced. This can be problematic in the heat of combat. By stark contrast, the ballistic material of the invention actually improves its stopping performance as projectiles are fired into it, because the accumulation of spent projectile material actually collects at about the same depth in the material, forming a plate of spent projectile material that helps to stop additional incoming projectiles. Thus, repeated firing into the same general region of the material in the hopes of eventually penetrating it has the opposite effect. As an example, an enemy combatant who repeatedly fires at the driver's compartment of an armored vehicle, or the cockpit of a helicopter gunship, in the hopes of disabling or killing the driver or pilot, actually renders the individual under attack safer.

What is claimed is:

1. A ballistic apparatus comprising:  
a polymeric material comprising a high molecular weight, high density polyethylene.
2. The ballistic apparatus of claim 1, wherein the polymeric material comprises at least one first region having a first density and at least one second region having a second density different from the first density.

**3.** The ballistic apparatus of claim 2, wherein the first and second regions are substantially along a path of a projectile fired at the apparatus.

**4.** The ballistic apparatus of claim 3, comprising:

(a) a relatively flat core of polymeric material having a first density, disposed within:

(b) a relatively flat shell of polymeric material having a second density, wherein the first density is higher than the second density.

**5.** The ballistic apparatus of claim 4, wherein the core comprises fused tubes of extruded polymeric material.

**6.** The ballistic apparatus of claim 4, wherein the shell comprises fused tubes of extruded polymeric material.

**7.** The ballistic apparatus of claim 4, further comprising a tumble zone disposed between the core and the shell, adapted to accumulate material from spent projectiles.

**8.** The ballistic apparatus of claim 1, wherein the polymeric material further comprises maleated high density polyethylene.

**9.** The ballistic apparatus of claim 1, wherein the polymeric material further comprises an inorganic fiber, sphere, or plate, comprising a metallic material, a ceramic material, or a combination thereof.

**10.** The ballistic apparatus of claim 9, wherein the inorganic fiber, sphere or plate comprises silica fibers.

**11.** The ballistic apparatus of claim 9, wherein the inorganic fiber, sphere or plate comprises metallic fibers.

**12.** The ballistic apparatus of claim 9, wherein inorganic fiber, sphere, or plate provides internal support to the apparatus.

**13.** The ballistic apparatus of claim 1, wherein the polymeric material further comprises TPO elastomers, TPV elastomers, or combinations thereof.

**14.** The ballistic material of claim 13, wherein the elastomer is selected from the group consisting of natural rubber, EPDM rubber, CPE (Chlorinated polyethylene), TPO, TPV, and combinations thereof.

**15.** The ballistic apparatus of claim 2, wherein the polymeric material further comprises an inorganic fiber, sphere, or plate, and an elastomer.

**16.** The ballistic apparatus of claim 15, wherein the inorganic fiber, sphere, or plate comprises a metallic fiber, a ceramic fiber, or a combination thereof.

**17.** The ballistic apparatus of claim 16, wherein the inorganic fiber, sphere or plate comprises silica fibers and the elastomer is selected from the group consisting of natural rubber, EPDM rubber, CPE (Chlorinated polyethylene), TPO, TPV and combinations thereof.

**18.** The ballistic apparatus of claim 17, wherein the material is fully vulcanized materials.

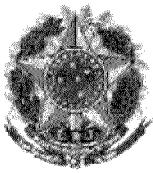
**19.** The ballistic apparatus of claim 1, wherein the ballistic apparatus is a firearm backstop.

**20.** The ballistic apparatus of claim 1, wherein the ballistic apparatus is protective ballistic armor.

**21.** A method of protecting a structure from ballistic impact, comprising disposing adjacent to the structure the ballistic apparatus of claim 1.

**22.** The method of claim 21, wherein the structure is selected from the group consisting of personnel, building structures, ground vehicles, aircraft, spacecraft, ships, and pipelines.

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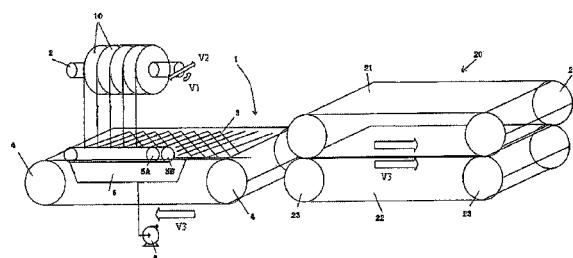
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(57) Resumo: FOLHA DE MATERIAL DE MÚLTIPLAS CAMADAS E PROCESSO PARA SUA PREPARAÇÃO. A invenção se refere a uma folha de material de múltiplas camadas compreendendo uma pilha consolidada de monocamadas unidirecionais de polímero estirado, pelo que difere a direção de estiramento de duas monocamadas subsequentes na pilha. Ao menos uma monocamada compreende uma pluralidade de fitas unidirecionais do polímero estirado, alinhadas na mesma direção, pelo que fitas adjacentes não se sobreponem. A invenção também se refere a um processo para a preparação da folha de material de múltiplas camadas, e a um artigo de resistência balística compreendo a folha de material de múltiplas camadas.



FOLHA DE MATERIAL DE MÚLTIPLAS CAMADAS E PROCESSO PARA SUA  
PREPARAÇÃO

A invenção se refere à folha de material de múltiplas camadas compreendendo uma pilha consolidada de monocamadas unidireccionais de polímero estirado, e ao seu processo de preparação. A invenção também se refere a um artigo de resistência balística compreendendo a folha de material de múltiplas camadas.

Uma folha de material de múltiplas camadas compreendendo uma pilha consolidada de monocamadas unidireccionais de polímero estirado é conhecida a partir da EP 1627719 A1. Essa publicação revela uma folha de material de múltiplas camadas compreendendo várias monocamadas unidireccionais; consistindo em polietileno de peso molecular ultra-elevado, e essencialmente destituído de matrizes de ligação, pelo que difere a direção de estiramento de duas monocamadas subsequentes na pilha. Uma monocamada do material de múltiplas camadas revelado na EP 1627719 A1 é produzida mediante posicionamento de uma pluralidade de fitas de polietileno de peso molecular ultra-elevado adjacentes umas às outras de modo que fitas adjacentemente posicionadas se sobreponem ao menos parcialmente ao longo de suas bordas laterais. Sem a sobreposição o material de múltiplas camadas, conhecido, não pode ser produzido. Além disso, para se obter boas propriedades antibalísticas, a folha de material da EP 1627719 A1 faz uso exclusivamente de polietileno de peso molecular ultra-elevado, essencialmente livre das matrizes de ligação.

Embora a folha de material de múltiplas camadas de

acordo com a EP 1627719 A1 mostre um desempenho balístico satisfatório, esse desempenho pode ser aperfeiçoado ainda mais.

O objetivo da presente invenção é o de prover uma folha de material de múltiplas camadas tendo ao menos propriedades antibalísticas similares como o material conhecido, e cuja folha pode ser facilmente produzida.

Esse objetivo é alcançado de acordo com a invenção mediante provisão de uma folha de material de múltiplas camadas compreendendo uma pilha consolidada de monocamadas unidirecionais de polímero estirado, pelo que a direção de estiramento de duas monocamadas subsequentes na pilha difere, de modo que ao menos uma monocamada compreende ao menos uma fita unidirecional do polímero estirado, cada fita compreende bordas longitudinais; com as quais a monocamada é livre de sobreposições, ou livre de uma área de espessura elevada, adjacente às bordas longitudinais, e ao longo do comprimento substancial das mesmas. Preferivelmente, a monocamada é livre de sobreposições, ou livre da área de espessura elevada adjacente e ao longo de ao menos 50%, 60%, 70%, 80%, 90% ou 95% do comprimento das bordas longitudinais da ao menos uma fita unidirecional. Mais preferivelmente, a monocamada é livre de sobreposições, ou livre de uma área de espessura elevada ao longo e adjacente do comprimento total das bordas longitudinais da ao menos uma fita unidirecional.

A formação das monocamadas que são livres de sobreposições ou níveis excessivos de aglutinantes permite que as monocamadas sejam facilmente empilhadas e comprimidas em uma folha de material de múltiplas camadas

com densidade areal uniforme resultando em um desempenho antibalístico mais homogêneo através da folha de material de múltiplas camadas.

Em uma modalidade da presente invenção, esse objetivo 5 é alcançado por intermédio de uma folha de material de múltiplas camadas e um processo para produzir tal folha de material de múltiplas camadas, a folha compreendendo uma pilha consolidada de monocamadas unidirecionais de polímero estirado, com as quais difere a direção de estiramento de 10 duas monocamadas subsequentes na pilha, com as quais ao menos uma monocamada compreende uma pluralidade de fitas unidirecionais do polímero estirado, alinhadas na mesma direção, e pelo que fitas adjacentes não se sobrepõem.

Verifica-se que uma folha de material de múltiplas 15 camadas de acordo com a invenção, isto é, uma folha em que áreas de espessura elevada adjacentes e ao longo das bordas longitudinais das fitas unidirecionais, por exemplo, sobreposições longitudinais de fitas ou fitas extensivamente ligadas em conjunto com material aglutinante 20 de sobreposição são substancialmente ausentes, não somente aperfeiçoando as propriedades antibalísticas da folha, mas fazendo isso em uma extensão inesperadamente elevada. Preferivelmente, a monocamada é livre de uma área de espessura elevada que se estende ao longo (mais 25 propriamente, transversalmente) e adjacentes às bordas longitudinais da ao menos uma fita unidirecional. A ocorrência de áreas de espessura elevada que se estendem ao longo das bordas longitudinais da fita unidirecional ou fitas unidirecionais, e adjacentes a elas, torna mais 30 difícil formar uma pilha consolidada homogênea em

comparação com as áreas de espessura elevada atribuídas à sobreposição transversal de fitas unidirecionais, de modo que observado quando as fitas são alinhadas de tal modo que elas formam uma estrutura tecida.

5       Uma folha de material de múltiplas camadas particularmente preferida de acordo com a invenção compreende uma pilha de monocamadas, pelo que cada monocamada é construída de uma pluralidade de fitas unidirecionais do polímero estirado alinhadas na mesma  
10      direção, e pelo que em cada monocamada as fitas adjacentes não se sobrepõem. Uma folha de material de acordo com a invenção é mais homogênea do que a folha de material conhecida. Na realidade, nos locais de sobreposição, a folha de material conhecida terá zonas de maior densidade  
15      areal. Essas zonas estão ausentes ou ocorrem em um grau menor na folha de material da invenção. Essa característica surpreendentemente aperfeiçoa as propriedades antibalísticas.

Uma monocamada da folha de material de múltiplas  
20      camadas da invenção é produzida preferivelmente mediante posicionamento de uma pluralidade de fitas com suas bordas longitudinais tão próximas quanto possível umas da outras, e preferivelmente em proximidade de toque. Contudo, para poder produzir uma monocamada em uma escala industrial em  
25      velocidades econômicas, seria desejável permitir uma folga entre as fitas adjacentes (isto é, as fitas adjacentes em uma monocamada não estão em contato ao longo de suas bordas longitudinais - folga maior do que 0%). Preferivelmente, a folha de material de acordo com a invenção é caracterizada  
30      em que a folga entre fitas adjacentes em uma monocamada é

menor do que 10% da largura das fitas unidirecionais adjacentes e, ainda mais preferivelmente, menor que 5%, ainda mais preferido 3% da largura das fitas unidirecionais adjacentes. Mais preferivelmente a folga entre as fitas 5 adjacentes em uma monocamada é menor do que 1%.

Uma folha de material de acordo com essa modalidade preferida é facilmente produzida e ainda assim apresenta propriedades antibalísticas de nível similar as das folhas de material sem folga. Embora uma monocamada de acordo com 10 a invenção seja preferivelmente produzida mediante posicionamento de uma pluralidade de fitas com suas bordas longitudinais umas contra as outras, as monocamadas construídas a partir de apenas uma fita (larga o suficiente) de largura suficiente também está dentro do 15 escopo da invenção, uma vez que tal monocamada não mostra áreas de espessura elevada adjacentes e ao longo da extensão das bordas longitudinais da ao menos uma fita unidirecional.

Mediante alinhamento das várias fitas de polímero 20 estirado de tal modo que cada fita esteja orientada em paralelo a fitas adjacentes, e de tal modo que uma quantidade substancial, isto é, ao menos 90% das fitas adjacentes não se sobrepõem, um desempenho antibalístico aperfeiçoado é alcançado através de materiais conhecidos. 25 De acordo com a técnica anterior, conforme descrito na EP 1627719 A1, as monocamadas unidirecionais compreendem uma pluralidade de fitas de polietileno unidirecionais de alta resistência, orientadas em paralelo em um plano, mas parcialmente sobrepostas, a área de sobreposição sendo da 30 ordem de 5 mm a 40 mm de largura. De acordo com uma

modalidade alternativa, uma película polimérica estreita, de aproximadamente 5 a 20 mm de largura, é colocada sobre a área de contato é colocada sobre a área de contato entre duas fitas adjacentes. Uma vantagem adicional da folha de material de múltiplas camadas de uma modalidade preferida da presente invenção é que não há necessidade de tais películas poliméricas adicionais para se obter boas propriedades antibalísticas. Além disso, pelo fato de se ter fitas que são livres de áreas de espessura elevada, conforme definido na presente invenção, o subsequente empilhamento e consolidação das monocamadas sob pressão resultará em uma densidade ou espessura areal mais homogênea na folha de material de múltiplas camadas em comparação com o estado da técnica.

Uma modalidade particularmente preferida da folha de material de múltiplas camadas de acordo com a invenção é caracterizada em que o polímero do qual ela é feita é selecionada do grupo consistindo em poliolefinas, poliésteres, alcoóis polivinílicos, poliacrilonitrilas, poliamidas, especialmente poli(p-fenileno tereftalamida), polímeros cristalinos líquidos e polímeros semelhantes à escada, tal como polibenzimidazol ou polibenzoazol, especialmente poli(1,4-fenileno-2,6-benzobisoxazol), ou poli(2,6-diimidazo[4,5-b-4',5'-e] piridinileno-1,4-(2,5-dihidroxi)fenileno). Fitas unidireccionais e monocamadas a partir desses polímeros são preferivelmente altamente orientadas mediante formas de material de estiramento, por exemplo, películas, em uma temperatura adequada. Com as fitas unidirectionais e monocamadas se quer dizer no contexto desse pedido fitas de monocamadas que mostram uma

orientação preferida das cadeias de polímero em uma direção, isto é, na direção do estiramento. Tais fitas e monocamadas podem ser produzidas mediante estiramento, preferivelmente por intermédio de estiramento uniaxial, e 5 apresentarão propriedades mecânicas anisotrópicas.

A folha de um material de múltiplas camadas da invenção permite o uso de polímeros estirados com resistência relativamente baixa e, portanto, não se precisa de polietileno de peso molecular ultra-elevado para se 10 obter desempenho antibalístico adequado. Contudo, uma sua modalidade preferida compreende polietileno de peso molecular ultra-elevado. O polietileno de peso molecular ultra-elevado pode ser linear ou ramificado, embora polietileno preferivelmente linear seja usado. O 15 polietileno linear é entendido aqui como significando polietileno com menos do que uma cadeia lateral por 100 a 100 átomos de carbono, e preferivelmente com menos do que uma cadeia lateral por 300 átomos de carbono; uma cadeia lateral ou ramificação geralmente contendo ao menos 10 20 átomos de carbono. As cadeias laterais podem ser medidas adequadamente por intermédio de FTIR em uma película moldada por compressão de 2 mm de espessura, conforme mencionado, por exemplo, na EP 0269151. O polietileno linear pode conter adicionalmente até 5 mols% de um ou mais alquenos diferentes que são copolimerizáveis com o mesmo, 25 tal como propeno, buteno, penteno, 4-metilpenteno, octeno. Preferivelmente, o polietileno linear é de elevada massa molar com uma viscosidade intrínseca (IV, conforme determinado em soluções em decalina a 135°C) de ao menos 4 30 dl/g; mais preferivelmente de ao menos 8 dl/g, mais

preferivelmente de ao menos 10 dl/g. Tal polietileno também é referido como polietileno de peso molecular ultra-elevado. Viscosidade intrínseca é uma medida para peso molecular que pode mais facilmente ser determinado do que parâmetros de massa molar, efetivos como Mn e Mw. Uma película de polietileno desse tipo produz propriedades antibalísticas particularmente adequadas.

As fitas de acordo com a invenção podem ser preparadas na forma de películas. Um processo preferido para formação de tais películas ou fitas compreende alimentar um pó polimérico entre uma combinação de correias sem fim, moldar por compressão o pó polimérico em uma temperatura abaixo do seu ponto de fusão e laminar o polímero moldado por compressão resultante seguido de estiramento. Tal processo, por exemplo, é descrito na EP 0 733 460 A2, o qual é aqui incorporado como referência. Se desejado, antes de alimentar e moldar por compressão o pó de polímero, o pó de polímero pode ser misturado com um composto orgânico líquido adequado tendo um ponto de ebulição superior ao ponto de fusão do polímero. Moldagem por compressão também pode ser realizada mediante retenção temporária do pó de polímero entre as correias sem fim enquanto transportando o mesmo. Isso pode ser feito, por exemplo, mediante provisão de pratos de prensar e/ou rolos em conexão com as correias sem fim. O polímero UHMWPE usado nesse processo precisa ser estirável no estado sólido.

Outro processo preferido para a formação de películas compreende alimentar um polímero a uma extrusora, extrudando uma película em uma temperatura acima do ponto e fusão da mesma e estirando a película de polímero

extrudada. Se desejado, antes de alimentar o polímero à extrusora, o polímero pode ser misturado com um composto orgânico líquido adequado, por exemplo, para formar um gel, tal como é preferivelmente o caso ao se utilizar 5 polietileno de peso molecular ultra-elevado.

Estiramento, preferivelmente estiramento uniaxial, das películas produzidas pode ser realizado por meio conhecido na técnica. Tal meio comprehende esticamento de extrusão e esticamento de tração em unidades de estiramento adequadas.

10 Para se obter resistência mecânica aumentada e rigidez, o estiramento pode ser realizado em múltiplas etapas. No caso das películas de polietileno de peso molecular ultra-elevado, preferidas, o estiramento é realizado tipicamente uniaxialmente em um número de etapas de estiramento. A 15 primeira etapa de estiramento pode, por exemplo, compreender estiramento até um fator de esticamento de 3. Estiramento múltiplo pode tipicamente resultar em um fator de esticamento de 9 para temperaturas de estiramento de até 120°C, um fator de esticamento de 25 para temperaturas de 20 estiramento de até 140°C, e um fator de esticamento de 50 para temperaturas de estiramento de até 150°C e acima. Mediante estiramento múltiplo em temperaturas crescentes, os fatores de esticamento de aproximadamente 50 e superiores podem ser alcançados. Isso resulta em fitas de 25 elevada resistência pelo que para fitas de polietileno de peso molecular ultra-elevado, resistências de 1.5 GPa a 1.8 GPa e superiores podem ser obtidos.

As fitas estiradas resultantes podem ser usadas como tal para produzir uma monocamada, ou elas podem ser 30 cortadas em sua largura desejada, ou divididas ao longo da

direção de estiramento. Preferivelmente, a monocamada é produzida a partir de fita que não é fendida. A largura das fitas unidireccionais assim produzidas é limitada apenas pela largura da película a partir da qual elas são produzidas. A largura das fitas preferivelmente é superior a 2 mm, mais preferivelmente superior a 5 mm e ainda mais preferivelmente superior a 30 mm. A densidade areal das fitas ou monocamadas pode ser variada através de uma grande faixa, por exemplo, entre 5 e 200 g/m<sup>2</sup>. Densidade areal preferida está entre 10 e 120 /m<sup>2</sup>, mais preferida entre 15 e 80 g/m<sup>2</sup> e mais preferida entre 20 e 60 g/m<sup>2</sup>.

Outra folha de material de múltiplas camadas particularmente preferida de acordo com a invenção compreende ao menos uma monocamada, preferivelmente todas as monocamadas, construídas de uma pluralidade de fitas unidireccionais do polímero estirado, alinhadas de tal modo que elas formam uma estrutura tecida. Tais fitas podem ser fabricadas mediante aplicação de técnicas têxteis, tal como tecelagem, entrelaçamento, etc. de pequenas tiras de polímero estirado em vez de fibras, o que normalmente é feito. Embora nessa modalidade as tiras de polímero tenham áreas de espessura elevada onde as tiras parcialmente se sobrepõem nos pontos de cruzamento, as áreas de espessura elevada cruzam as bordas longitudinais da fita unidirecional, mais propriamente do que se estendem ao longo e adjacentes às bordas longitudinais. Cada fita (sendo um tecido trançado de pequenas tiras) é posicionada de tal modo que não ocorre sobreposição entre fitas adjacentes, alinhadas na mesma direção. Mediante empilhamento das fitas de tal modo que as linhas de emenda

em diferentes monocamadas são escalonadas com relação umas às outras, propriedades antibalísticas são adicionalmente aperfeiçoadas.

Em algumas modalidades, a monocamada pode incluir um aglutinante o qual é aplicado localmente para ligar e estabilizar as várias fitas unidireccionais de tal modo que a estrutura da monocamada é mantida durante manejo e fabricação de folhas unidireccionais. Aglutinantes adequados são descritos, por exemplo, na EP 0191306 B1, EP 1170925 A1, EP 0683374 B1 e EP 1144740 A1. O aglutinante pode ser aplicado em várias formas e modos; por exemplo, como uma tira de ligação transversal (transversal com relação às fitas unidireccionais). A aplicação do aglutinante durante a formação da monocamada vantajosamente estabiliza as fitas, desse modo possibilitando que ciclos de produção mais rápidos sejam obtidos enquanto evitando sobreposições entre fitas adjacentes.

Em uma modalidade, um aglutinante é aplicado para encostar fixamente fitas unidireccionais adjacentes ao longo de suas bordas longitudinais. Como a função do aglutinante é de temporariamente reter e estabilizar a pluralidade de fitas unidireccionais durante manejo e fabricação de folhas unidireccionais, a aplicação localizada do aglutinante é preferida. Aplicação local do aglutinante é aplicação que é limitada às proximidades imediatas das bordas longitudinais e pode incluir aplicação localizada intermitente (aplicação de pontos ao longo das bordas longitudinais).

Preferivelmente, a aplicação do aglutinante resulta em uma espessura elevada máxima da monocamada (borda em relevo) de 150% da espessura média das fitas unidireccionais

formando a monocamada. Mais preferivelmente, a aplicação do aglutinante resulta em uma espessura elevada máxima de 120%, 110% ou 105% da espessura média da pluralidade de fitas unidireccionais formando a monocamada. Em outra 5 modalidade, a aplicação do aglutinante resulta em um aumento na espessura da monocamada adjacente às bordas longitudinais das fitas unidireccionais de menos do que 4 micrômetros, mais preferivelmente menos do que 3, 2 ou 1 micrômetro.

10 Em modalidades com aplicação localizada intermitente do aglutinante, a proporção das bordas longitudinais compreendendo aglutinante é preferivelmente menor do que 50%, 30%, 20%, 10%, 5% ou 2%. Similarmente, a proporção das bordas longitudinais (ou áreas adjacentes às bordas 15 longitudinais) da fita unidirecional a qual está em relevo devido aplicação do aglutinante é preferivelmente inferior a 50%, 30%, 20%, 10%, 5% ou 2%. Preferivelmente, o aglutinante compreende menos do que 20%, 10%, 5%, 2%, 1%, 0,5% ou 0,2% do peso da pilha consolidada ou de monocamada.

20 Em modalidades alternativas, um meio de aglutinação, tal como solda ultra-sônica, pode ser usado para fundir intermitentemente as seções das bordas longitudinais das fitas unidireccionais adjacentes em conjunto.

Com fitas unidireccionais adjacentes dentro de uma 25 monocamada intermitentemente ligada ao longo de bordas longitudinais contíguas, as fitas unidireccionais adjacentes são mantidas em um arranjo paralelo. A aplicação do aglutinante permite que as fitas unidireccionais adjacentes estejam próximas sem sobreposição substancial das bordas 30 longitudinais contíguas. A variação localizada de espessura

da monocamada é vantajosamente reduzida (em comparação com as monocamadas convencionais com bordas longitudinais sobrepostas ou com tiras de aglutinação polimérica, sobrepostas, contínuas) o que contribui para uma pilha 5 consolidada resultante de monocamadas com uma espessura mais homogênea e, portanto, distribuição de tensão.

A espessura das monocamadas ou fitas da folha de material de múltiplas camadas pode, em princípio, ser selecionada dentro de faixas amplas. Preferivelmente, 10 contudo, a folha de material de múltiplas camadas de acordo com a invenção é caracterizada em que a espessura de ao menos uma monocamada não excede 120  $\mu\text{m}$ , mais preferivelmente não excede 50  $\mu\text{m}$ , e mais preferivelmente está compreendida entre 5 e 29  $\mu\text{m}$ . Propriedades 15 antibalísticas particularmente adequadas são obtidas se a espessura de todas as monocamadas da pilha não exceder 120  $\mu\text{m}$ , mais preferivelmente não exceder 50  $\mu\text{m}$ , e mais preferivelmente está compreendida entre 3 e 29  $\mu\text{m}$ . Uma folha de material de múltiplas camadas preferida adicional 20 de acordo com a invenção é caracterizada em que a espessura da ao menos uma monocamada superior a 10  $\mu\text{m}$  e não excedendo 50  $\mu\text{m}$ , preferivelmente não excedendo 100  $\mu\text{m}$  ou mais preferivelmente não excedendo 120  $\mu\text{m}$ . Mediante limitação da espessura de ao menos uma das monocamadas na pilha à 25 espessura reivindicada, propriedades antibalísticas suficientes são obtidas surpreendentemente mesmo com as monocamadas tendo resistências mais propriamente limitadas.

A resistência das fitas na folha de material de múltiplas camadas depende amplamente do polímero a partir 30 do qual elas são produzidas, e da sua razão de esticamento

(uniaxial). A resistência das fitas (e monocamadas) é de ao menos 0.75 GPa, preferivelmente de ao menos 0.9 GPa, mais preferivelmente de ao menos 1.2 GPa, ainda mais preferivelmente de ao menos 1.5 Gpa, ainda mais preferivelmente de ao menos 1.8 GPa, e ainda mais preferivelmente de ao menos 2.1 GPa, e mais preferivelmente de ao menos 3 GPa. As monocamadas unidirecionais são preferivelmente interconectadas suficientemente umas às outras, significando que as monocamadas unidirecionais não se desprendem sob condições de uso normal tal como, por exemplo, em temperatura ambiente.

A folha de material de múltiplas camadas de acordo com a invenção compreende pelo menos duas monocamadas unidirecionais, preferivelmente ao menos 4 monocamadas unidirecionais, mais preferivelmente ao menos 6 monocamadas unidirecionais, ainda mais preferivelmente ao menos 8 monocamadas unidirecionais e mais preferivelmente ao menos 10 monocamadas unidirecionais. Aumentar o número de monocamadas unidirecionais na folha de material de múltiplas camadas da invenção simplifica a fabricação dos artigos a partir dessas folhas de material, por exemplo, chapas antibalísticas.

Em uma modalidade da presente invenção, é provido um processo para a preparação de uma folha de material de múltiplas camadas compreendendo:

(a) posicionar uma primeira fita unidirecional de ao menos um polímero estirado sobre um substrato móvel desse modo formando uma primeira monocamada, pelo que a monocamada é livre de uma área de espessura elevada adjacente e ao longo do comprimento substancial das bordas

longitudinais da ao menos uma fita unidirecional;

(b) segurar a primeira monocamada sobre o substrato móvel;

5 (c) posicionar uma segunda fita unidirecional de ao menos um polímero estirado sobre a primeira monocamada, desse modo formando uma segunda monocamada, pelo que a direção da segunda monocamada faz um ângulo  $\alpha$  com relação à primeira; e

10 (d) comprimir a pilha assim formada para consolidar as suas monocamadas. A pilha consolidada de monocamadas tem espessura mais homogênea/densidade areal em comparação com a técnica anterior, devido à redução ou ausência de áreas de espessura elevada ao longo e adjacente às bordas longitudinais da ao menos uma fita unidirecional,  
15 preferivelmente, em cada uma das monocamadas.

Em uma modalidade preferida da presente invenção, é provido um processo para a preparação de uma folha de material de múltiplas camadas do tipo reivindicado. O processo de acordo com a invenção comprehende as etapas de:

20 (a) prover uma pluralidade de fitas de polímero estirado, alinhadas de tal modo que cada fita é orientada em paralelo às fitas adjacentes, e pelo que as fitas adjacentes não se sobreponem substancialmente;

25 (b) posicionar as várias fitas de polímero estirado sobre um substrato móvel desse modo formando uma primeira monocamada;

(c) segurar a primeira monocamada sobre o substrato móvel;

30 (d) posicionar uma pluralidade de fitas de polímero estirado sobre a primeira monocamada, desse modo formando

uma segunda monocamada, pelo que a direção da segunda monocamada faz um ângulo  $\alpha$  com relação à primeira; e

(e) comprimir a pilha assim formada para consolidar as suas monocamadas.

5 A etapa (a) pode incluir opcionalmente a aplicação de um aglutinante ou meio de aglutinação para reter ou estabilizar as fitas adjacentes, de tal modo que velocidades de produção aumentadas podem ser conseguidas. Com o processo reivindicado, uma folha de material de 10 múltiplas camadas substancialmente destituída de regiões sobrepostas, isto é, regiões com maior densidade areal, podem ser facilmente produzidas. Folhas de material dessa forma produzidas têm propriedades antibalísticas aperfeiçoadas com relação a uma folha de material com 15 regiões de sobreposição.

Preferivelmente, a pluralidade de fitas de polímero estirado é desenrolada a partir de uma estação de desenrolamento e a etapa (d) é realizada mediante dobradura das várias fitas de polímero estirado ao menos parcialmente 20 sobre elas próprias. Mais especificamente, as várias fitas de polímero estirado são posicionadas de tal modo que a primeira monocamada forma um ângulo  $\beta$  com relação à direção de movimento do substrato, e a dobradura é realizada de tal modo que a linha de dobra se estende aproximadamente 25 paralelo à direção de movimento do substrato. O processo de acordo com a invenção é caracterizado ainda em que o ângulo  $\beta$  está entre 40 e 50 graus, pelo que o ângulo  $\beta$  mais preferido é de aproximadamente 45 graus.

Outro processo preferido de acordo com a invenção é 30 caracterizado em que a segunda monocamada é ao menos

parcialmente aderida à primeira monocamada. Isso pode ser facilmente realizado por intermédio de soldagem ultrassônica, adição de uma película de baixa fusão, um adesivo, ou mediante qualquer outro método de unir as camadas. A 5 aderência da segunda monocamada à primeira monocamada é preferivelmente suficientemente forte para permitir o transporte do conjunto de monocamadas, sem movimento relativo, substancial, das fitas separadas e/ou das monocamadas.

10 De acordo com o processo da invenção, uma folha de material de múltiplas camadas é produzida em que a direção de retirada de duas monocamadas subsequentes na pilha difere em um ângulo  $\alpha$ . Para o processo preferido no qual a linha de dobra se estende aproximadamente paralela à direção do movimento do substrato, o ângulo  $\alpha - 2\beta$ . Embora o ângulo  $\alpha$  possa ser selecionado dentro de amplas faixas, o ângulo  $\alpha$  está preferivelmente entre 45 e 135°, mais preferivelmente entre 65 e 115° e ainda mais preferivelmente entre 80 e 100°. Na faixa preferida 15 mencionada por último um ângulo particularmente preferido  $\alpha$  é de aproximadamente 90°. Um material produzido de acordo com essa modalidade preferida é denotado como camada transversal na técnica.

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A folha de material de múltiplas camadas de acordo com 25 a invenção é particularmente útil na fabricação de artigos resistentes à balística, tal como trajes ou chapas blindadas. Aplicações balísticas compreendem aplicações com ameaça balística de projéteis de vários tipos incluindo os assim chamados projéteis AP, de perfuração de blindagem, e 30 partículas duras tal como, fragmentos e estilhaços de

metralha.

O artigo de resistência balística de acordo com a invenção compreende ao menos duas monocamadas unidireccionais, preferivelmente ao menos 10 monocamadas unidireccionais, mais preferivelmente ao menos 20 monocamadas unidireccionais, ainda mais preferivelmente ao menos 30 monocamadas unidireccionais e mais preferivelmente ao menos 40 monocamadas unidireccionais. A direção de tiragem de duas monocamadas subsequentes na pilha difere em 5 um ângulo  $\alpha$ . O ângulo  $\alpha$  está preferivelmente entre 45 e 10 135°, mais preferivelmente entre 65 e 115° e mais preferivelmente entre 80 e 100°.

Preferivelmente o artigo de resistência balística de acordo com a invenção compreende uma folha adicional de 15 material inorgânico selecionado do grupo consistindo em cerâmica; metal, preferivelmente alumínio, magnésio-titânio, níquel, cromo e ferro ou suas ligas; vidro; grafite, ou combinações dos mesmos. Particularmente preferido é o metal. Em tal caso o metal na folha de metal 20 tem preferivelmente um ponto de fusão de ao menos 350°C, mais preferivelmente de ao menos 500°C, mais preferivelmente de ao menos 600°C. Metais adequados incluem alumínio, magnésio, titânio, cobre, níquel, cromo, berílio, ferro e cobre incluindo suas ligas como, por exemplo, aço e 25 aço inoxidável e ligas de alumínio com magnésio (assim chamado alumínio da série 5000), e ligas de alumínio com zinco e magnésio ou com zinco, magnésio e cobre (assim chamado alumínio da série 7000). Nas ligas a quantidade, por exemplo, de alumínio, magnésio, titânio e ferro é 30 preferivelmente de ao menos 50% em peso. Folhas de metal

preferidas compreendendo alumínio, magnésio, titânio, níquel, cromo, berílio, ferro incluindo suas ligas. Mais preferivelmente a folha de metal se baseia em alumínio, magnésio, titânio, níquel, cromo, ferro e suas ligas. Isso 5 resulta em um artigo antibalístico leve com boa durabilidade. Ainda mais preferivelmente o ferro e suas ligas na folha de metal têm uma dureza Brinell de ao menos 500. Mais preferivelmente a folha de metal se baseia em alumínio, magnésio, titânio, e suas ligas. Isso resulta no 10 artigo antibalístico mais leve com a mais elevada durabilidade. Durabilidade nesse pedido significa a vida útil de um composto sob condições de exposição ao calor, umidade luz e irradiação UV. Embora a folha adicional de material possa ser posicionada em qualquer lugar na pilha 15 de monocamadas, o artigo de resistência balística preferido é caracterizado em que a folha adicional de material é posicionada no lado externo da pilha de monocamadas, mais preferivelmente ao menos na sua face de impacto.

O artigo de resistência balística de acordo com a 20 invenção compreende preferivelmente uma folha adicional do material inorgânico descrito acima tendo uma espessura de no máximo 100 mm. Preferivelmente a espessura máxima da folha adicional de material inorgânico é de 75 mm, mais preferivelmente 50 mm, e mais preferivelmente de 25 mm. 25 Isso resulta no melhor equilíbrio entre o peso e as propriedades antibalísticas. Preferivelmente, no caso da folha adicional de material inorgânico ser uma folha de metal, a espessura da folha de metal, é de ao menos 0,25 mm, mais preferivelmente e ao menos 0,5 mm, e mais 30 preferivelmente de ao menos 0,75 mm. Isso resulta em um

desempenho antibalístico ainda melhor.

A folha adicional de material inorgânico pode ser opcionalmente pré-tratada para melhorar a adesão com a folha de material de múltiplas camadas. Pré-tratamento 5 adequado da folha adicional inclui tratamento mecânico, por exemplo, tornar áspera ou limpar da sua superfície mediante areação ou esmerilhamento, gravação química com, por exemplo, ácido nítrico e laminação com película de polietileno.

10 Em outra modalidade do artigo de resistência balística uma camada de ligação, por exemplo, um adesivo, pode ser aplicado entre a folha adicional e a folha de material de múltiplas camadas. Tal adesivo pode compreender uma resina de epóxi, uma resina de poliéster, uma resina de 15 poliuretano ou uma resina e vinil éster. Em outra modalidade preferida, a camada de ligação pode compreender ainda uma camada tecida ou não-tecida de fibra inorgânica, por exemplo, fibra de vidro ou fibra de carbono. Também é possível fixar a folha adicional à folha de material de 20 múltiplas camadas mediante meio mecânico, tal como, por exemplo, parafusos, pinos e encaixes de pressão. No caso em que o artigo de resistência balística de acordo com a invenção é usado em aplicações balísticas onde ameaça de projéteis AP, fragmentos ou dispositivos explosivos 25 improvisados podem ser encontrados a folha adicional é compreendida preferivelmente de uma folha de metal coberta com uma camada de cerâmica. Desse modo um artigo antibalístico é obtido com uma estrutura em camadas como a seguir: camada de cerâmica/folha de metal/ao menos duas 30 folhas unidireccionais com a direção das fibras na folha

unidirecional em um ângulo α em relação à direção das fibras em uma folha unidirecional adjacente. Materiais cerâmicos adequados incluem, por exemplo, óxido de alumina, óxido de titânio, óxido de silício, carboneto de silício e 5 carboneto de boro. A espessura da camada de cerâmica depende do nível de ameaça balística, mas geralmente varia entre 2 mm e 30 mm. Esse artigo de resistência balística é preferivelmente posicionado de tal modo que a camada de cerâmica está voltada para a ameaça balística.

10 Em uma modalidade da presente invenção, é provido um processo para fabricação de um artigo de resistência balística compreendendo:

(a) empilhar ao menos duas monocamadas de polímero estirado unidirecionais, cada monocamada compreendendo ao 15 menos uma fita unidirecional, pelo que a direção de estiramento das 2 monocamadas subseqüentes na pilha difere, pelo que ao menos uma camada está livre de uma área de espessura elevada adjacente e ao longo do comprimento substancial das bordas longitudinais da ao menos uma fita 20 unidirecional; e uma folha de material selecionada do grupo consistindo em cerâmica, aço, alumínio, titânio, vidro e grafite, ou combinações dos mesmos; e

(b) consolidar as folhas empilhadas sob temperatura e pressão.

25 Em uma modalidade preferida da presente invenção é provido um processo para a fabricação de um artigo de resistência balística compreendendo as etapas de:

(a) empilhar ao menos duas monocamadas de polímero estirado unidirecionais, pelo que a direção de estiramento 30 das duas monocamadas subseqüentes na pilha difere, pelo que

ao menos uma monocamada, e preferivelmente todas as monocamadas, compreende uma pluralidade de fitas unidireccionais do polímero estirado, alinhadas na mesma direção, pelo que fitas adjacentes não se sobrepõem, e uma 5 folha adicional de material inorgânico selecionado do grupo consistindo em cerâmica, aço, alumínio, titânio, vidro e grafite, ou combinações dos mesmos; e

(b) consolidar as folhas empilhadas sob temperatura e pressão.

10 Em um processo alternativo a pilha de ao menos duas monocamadas unidireccionais de polímero estirado foi fabricada em um processo separado, tal como descrito acima. Essa pilha pré-fabricada é então combinada com a folha adicional de material selecionado do grupo consistindo em 15 cerâmica, aço, alumínio, titânio, vidro e grafite, ou combinações dos mesmos, na etapa (a) do processo.

A consolidação para todos os processos descritos acima pode ser feita adequadamente em uma prensa hidráulica. Consolidação pretende significar que as monocamadas são 20 fixadas de forma relativamente firme umas às outras para formar uma unidade. A temperatura durante a consolidação geralmente é controlada através da temperatura da prensa. Uma temperatura mínima geralmente é escolhida de tal modo que uma velocidade de consolidação razoável é obtida. A 25 esse respeito 80°C é um limite de temperatura inferior adequado, preferivelmente esse limite inferior é de ao menos 100°C, mais preferivelmente de ao menos 120°C, mais preferivelmente de ao menos 140°C. Uma temperatura máxima é escolhida abaixo da temperatura na qual as monocamadas de 30 polímero estirado perdem suas elevadas propriedades

mecânicas devido, por exemplo, à fusão. Preferivelmente a temperatura é de ao menos 10°C, preferivelmente de ao menos 15°C e ainda mais preferivelmente de ao menos 20°C abaixo da temperatura de fusão da monocamada de polímero estirado.

5 No caso da monocamada de polímero estirado não exibir uma temperatura de fusão evidente, a temperatura na qual a monocamada de polímero estirado começa a perder suas propriedades mecânicas deve ser lida em vez da temperatura de fusão. No caso do polietileno de peso molecular ultra-  
10 elevado preferido, uma temperatura abaixo de 145°C geralmente será escolhida. A pressão durante a consolidação preferivelmente é de ao menos 7 MPa, mais preferivelmente de ao menos 15 MPa. Desse modo obtém-se um artigo antibalístico rígido. O tempo ótimo para consolidação  
15 geralmente varia de 5 a 120 minutos, dependendo das condições tal como temperatura, pressão e espessura da peça e pode ser verificado através de experimento de rotina. No caso em que artigos antibalísticos curvos devem ser produzidos, pode ser vantajoso em primeiro lugar pré-  
20 modelar a folha adicional de material no formato desejado, seguido pela consolidação com as monocamadas e/ou folha de material de múltiplas camadas.

Preferivelmente, para se obter uma elevada resistência balística, esfriamento após moldagem por compressão em alta  
25 temperatura é realizada também sob pressão. Pressão é preferivelmente mantida ao menos até que a temperatura esteja suficientemente baixa para prevenir relaxamento. Essa temperatura pode ser estabelecida por aqueles versados na técnica. Quando um artigo de resistência balística  
30 compreendendo monocamadas de polietileno de peso molecular

ultra-elevado é fabricado, temperaturas de compressão típicas variam de 90 a 150°C, preferivelmente de 115 a 130°C. Pressões de compressão típicas variam entre 100 a 300 bares, preferivelmente 100 a 180 bares, mais 5 preferivelmente 120 a 160 bares, enquanto que os tempos de compressão estão tipicamente entre 40 a 180 minutos.

A folha de material de múltiplas camadas e o artigo antibalístico da presente invenção são particularmente vantajosos em relação aos materiais antibalísticos 10 anteriormente conhecidos uma vez que eles proporcionam ao menos o mesmo nível de proteção que os artigos conhecidos em um peso significativamente inferior, ou um desempenho balístico aperfeiçoado em peso igual em comparação o artigo conhecido. Materiais de partida são não-dispendiosos e o 15 processo de fabricação é relativamente curto e desse modo eficaz em termos de custo. Como polímeros diferentes podem ser usados para produzir a folha de material de múltiplas camadas da invenção, as propriedades podem ser otimizadas de acordo com aplicação específica. Além de resistência 20 balística, as propriedades incluem, por exemplo, estabilidade térmica, durabilidade em prateleira, resistência à deformação, capacidade de ligação com outras folhas de material, propriedade de modelagem, e assim por diante.

25 A invenção será explicada agora adicionalmente por intermédio das figuras 1-4 a seguir sem, contudo, ser limitada a elas.

A Figura 1 representa esquematicamente uma modalidade de um aparelho para realizar o processo de acordo com a 30 invenção.

A Figura 2 representa esquematicamente uma folha de material de múltiplas camadas.

A Figura 3 representa esquematicamente uma monocamada de fitas tecidas.

5 A Figura 4 representa esquematicamente uma folha de material de múltiplas camadas.

Com referência à Figura 1, um aparelho 1 para produzir uma folha de material de múltiplas camadas do tipo reivindicado é mostrado. O aparelho compreende meio 2 para prover uma pluralidade de fitas de polímero estirado 10. O meio 2 pode, por exemplo, compreender uma estação de desenrolamento para rolos de fitas de polímero 10. As fitas de polímero 10 são alinhadas de tal modo que cada fita 10 é orientada em paralelo às fitas adjacentes 10. O aparelho 1 compreende ainda um substrato móvel 3, o qual, na modalidade mostrada é uma correia, acionada por dois rolos cilíndricos 4. A correia 3 é móvel em uma velocidade V3 na direção mostrada pela seta. As várias fitas 10 são posicionadas sobre o substrato 3 mediante passagem das fitas 10 através de um conjunto de rolos de passe (5a, 5b). As várias fitas 10 são seguras sobre o substrato 3 mediante meio de retenção, por exemplo, mediante perfuração do substrato 3, e proporcionando um espaço 6, o qual pode ser colocado sob vácuo pela bomba 7 abaixo do substrato 3. 25 Atrás do substrato móvel 3, uma prensa de correia 20 é posicionada, compreendendo duas superfícies aquecidas (21, 22), acionadas pelos rolos cilíndricos 23.

O processo de acordo com a invenção compreende desenrolar uma pluralidade de fitas de polímero estirado 30 não axialmente 10 a partir da estação de desenrolamento 2

em uma velocidade V1. As fitas 10 são posicionadas de tal modo que fitas adjacentes não se sobrepõem substancialmente, e não existem substancialmente folgas (tipicamente menos do que 2 mm) entre fitas adjacentes. As 5 fitas 10 são então alimentadas através do conjunto de rolos de passe (5a, 5b). Conforme mostrado na Figura 1, o conjunto de dispositivo de desenrolamento 2 e conjunto de rolos de passe (5a, 5b) se desloca para cima e para baixo do substrato 3 na direção transversal em uma velocidade V2.

10 O substrato de correia sob vácuo 3 se desloca em uma velocidade V3 em uma direção essencialmente perpendicular à direção transversal. A razão entre V2 e V3 é escolhida de tal modo que as várias fitas 10 são posicionadas sobre o substrato móvel 3 em um ângulo de aproximadamente 45 graus 15 com relação à direção de movimento do substrato 3, desse modo formando uma primeira monocamada. A primeira monocamada é segura sobre o substrato móvel 3 por intermédio da succção produzida pelo meio de vácuo (6, 7).

20 Quando o dispositivo de desenrolar 2 alcança o lado do substrato móvel 3, sua direção de movimento é invertida, e o dispositivo de desenrolar 2 se desloca na direção oposta. Desse modo, as várias fitas de polímero estirado 10 são dobradas parcialmente sobre elas próprias. Mais especificamente, as várias fitas de polímero estirado 10 25 são dobradas de tal modo que a linha de dobra se estende aproximadamente paralela à direção de movimento do substrato 3. Desse modo uma segunda monocamada é posicionada sobre a primeira monocamada, pelo que a direção da segunda monocamada faz um ângulo de aproximadamente 90 30 graus com relação à primeira monocamada. Para garantir que

o conjunto de primeira e segunda monocamada possa ser transportado sem movimento relativo das fitas separadas e/ou monocamadas, a segunda monocamada de fitas é aderida à primeira monocamada ao menos parcialmente. Meio adequado para fazer isso inclui, mas não é limitado à solda ultrassônica, adição de uma película de baixa fusão, um adesivo, um adesivo termofusível, ou qualquer outro método de unir as camadas.

Finalmente, o conjunto assim formado de monocamadas é alimentado a uma prensa de correia ou calandra 20 para consolidação final da folha de material de múltiplas camadas. Na prensa de correia ou calandra 20 as várias fitas empilhadas são ligadas em uma temperatura próxima ao ponto de fusão das fitas. O material de múltiplas camadas resultante é na modalidade descrita um material de duas camadas, de dobras transversais, feito de fitas, com a direção das fitas em um ângulo de aproximadamente 45 graus em relação à direção de movimento do substrato 3.

A largura das várias fitas 10 no dispositivo 2 é determinada pela largura do material de múltiplas camadas no substrato 3 que deve ser posicionado sobre a prensa de correia ou calandra 20. No caso em que o ângulo  $\beta$  das fitas com a direção de movimento do substrato 3 é de  $45^\circ$ , a largura das várias fitas 10 é a largura  $\sqrt{2}^*$  do material de múltiplas camadas.

Com referência à Figura 2, é mostrada uma apresentação gráfica da folha de material de múltiplas camadas de acordo com a invenção compreendendo uma pilha consolidada de duas monocamadas unidireccionais de polímero estirado, pelo que a direção de tiragem de duas monocamadas subsequentes na

pilha é girada em 90°, pelo que cada monocamada compreende uma pluralidade de fitas unidireccionais do polímero estirado alinhado na mesma direção, pelo que fitas adjacentes não se sobrepõem. Por razões de clareza, as 5 fitas individuais se estendem nas bordas da folha de material de múltiplas camadas.

Com referência à Figura 3, é mostrada uma apresentação gráfica de uma monocamada de acordo com a invenção pelo que a monocamada é construída de uma pluralidade de fitas unidireccionais do polímero estirado, alinhadas de modo que elas formam uma estrutura tecida.

Com referência à Figura 4, é mostrada uma apresentação gráfica de uma folha de material de múltiplas camadas de acordo com a invenção compreendendo a monocamada da Figura 15 3 denotada pelo numeral 1 (em linhas cheias), com abaixo da mesma uma segunda monocamada de fitas tecidas denotadas pelo numeral 2 (em linhas pontilhadas). A segunda monocamada é posicionada de tal modo que as linhas de emenda das monocamadas respectivas são alinhadas e uma 20 forma escalonada.

Os métodos de teste conforme referidos no presente pedido são como a seguir

- Viscosidade Intrínseca (IV) é determinada de acordo com o método PTC-179 (Hercules Inc. Rev. 29 de abril 25 de 1982) a 135°C em decalina, o tempo de dissolução sendo de 16 horas, com DBPC como antioxidante em uma quantidade de 2 g/l de solução, mediante extração da viscosidade conforme medido em diferentes concentrações para concentração zero;

30           • Propriedades de tração (medidas a 25°C) :

resistência à tração (ou resistência), módulo de tensão (ou módulo) e alongamento em ruptura (ou eab) são definidos e determinados em fios de multifilamentos conforme especificado em ASTM D885M, utilizando um comprimento 5 padrão nominal da fibra e 500 mm, uma velocidade de cruzeta de 50%/minuto. Com base na curva de tensão-esforço medida o módulo é determinado como o gradiente entre 0,3 e 1% de tensão. Para cálculo do módulo e resistências, as forças de tração medidas são divididas pela titulação, conforme 10 determinado mediante pesagem de 10 metros de fibra; valores em GPa são calculados supondo uma densidade de 0,97 g/cm<sup>3</sup>. As propriedades de tração dessas películas são medidas de acordo com ISO 1184 (H).

## REIVINDICAÇÕES

1. Folha de material de múltiplas camadas caracterizada por compreender uma pilha consolidada de monocamadas unidirecionais de polímero estirado, por meio das quais difere a direção de tiragem de duas monocamadas subseqüentes na pilha, por meio das quais ao menos uma monocamada compreende ao menos uma fita unidirecional do polímero estirado, cada fita compreende bordas longitudinais, pelo que a monocamada é livre de uma área de espessura elevada ao longo do e adjacente ao comprimento substancial das bordas longitudinais da ao menos uma fita unidirecional.

2. Folha de material de múltiplas camadas, de acordo com a reivindicação 1, caracterizada pelo fato de que a área de espessura elevada é ao menos 4 micrômetros maior do que a espessura de ao menos uma fita unidirecional.

3. Folha de material de múltiplas camadas, de acordo com a reivindicação 1, caracterizada pelo fato de que a área de espessura elevada é ao menos 50% maior do que a espessura da ao menos uma fita unidirecional.

4. Folha de material de múltiplas camadas, de acordo com qualquer uma das reivindicações 1, 2 ou 3, caracterizada pelo fato de que ao menos uma monocamada é livre de uma área de espessura elevada ao longo do e adjacente ao comprimento total das bordas longitudinais da ao menos uma fita unidirecional.

5. Folha de material de múltiplas camadas, de acordo com a reivindicação 1, 2, 3 ou 4, caracterizada pelo fato de que ao menos uma monocamada é construída de uma pluralidade de fitas unidirecionais do polímero estirado,

alinhas na mesma direção, pelo que as fitas adjacentes não se sobrepõem.

6. Folha de material de múltiplas camadas, de acordo com a reivindicação 5, caracterizada pelo fato de que ao 5 menos uma monocamada comprehende uma pluralidade de fitas unidirecionais do polímero estirado e em que a folga entre fitas adjacentes é menor do que 10% da largura das fitas unidirecionais adjacentes.

7. Folha de material de múltiplas camadas, de acordo 10 com a reivindicação 6, caracterizada pelo fato de que a folga entre fitas adjacentes é menor do que 5% da largura das fitas unidirecionais adjacentes.

8. Folha de material de múltiplas camadas, de acordo com a reivindicação 5, caracterizada pelo fato de que as 15 bordas longitudinais das fitas adjacentes se encostam, pelo menos parcialmente, umas nas outras.

9. Folha de material de múltiplas camadas, de acordo com a reivindicação 8, caracterizada pelo fato de que as fitas adjacentes se encostam, ao menos parcialmente 20 fixamente, umas nas outras.

10. Folha de material de múltiplas camadas, de acordo com qualquer uma das reivindicações 1, 2, 3, 4, 5, 6, 7, 8 ou 9, caracterizada pelo fato de que a espessura de ao menos uma monocamada não excede 100 micrômetros.

25 11. Folha de material de múltiplas camadas, de acordo com a reivindicação 10, caracterizada pelo fato de que a espessura de ao menos uma monocamada não excede 29 micrômetros.

30 12. Folha de material de múltiplas camadas, de acordo com a reivindicação 10 ou 11, caracterizada pelo fato de

que a espessura de ao menos uma camada é superior a 10 micrômetros.

13. Folha de material de múltiplas camadas, de acordo com qualquer uma das reivindicações 1, 2, 3, 4, 5, 6, 7, 8, 5 9, 10, 11 ou 12, caracterizada pelo fato de que a resistência de ao menos uma monocamada é de pelo menos 0.9 GPa.

14. Folha de material de múltiplas camadas, de acordo com a reivindicação 13, caracterizada pelo fato de que a 10 resistência de ao menos uma monocamada é de pelo menos 1.5 GPa.

15. Folha de material de múltiplas camadas, de acordo com qualquer uma das reivindicações 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13 ou 14, caracterizada pelo fato de que o 15 polímero é selecionado do grupo consistindo em poliolefinas, poliésteres, alcoóis polivinílicos, poliacrilonitrilas, poliamidas, especialmente poli(tereftalamida de p-fenileno), polímeros cristalinos líquidos e polímeros semelhantes à escada, tal como 20 polibenzimidazol ou polibenzoxazol, especialmente poli(1,4-fenileno-2,6-benzobisoxazol), ou poli(2,6-diimidazo[4,5-b-4',5'-e]piridinileno-1,4-(2,5-dihidroxi)fenileno).

16. Folha de material de múltiplas camadas, de acordo com a reivindicação 15, caracterizada pelo fato de que a 25 poliolefina compreende polietileno de peso molecular ultra-elevado.

17. Processo para preparação de uma folha de material de múltiplas camadas, de acordo com qualquer uma das reivindicações 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15 ou 16, 30 caracterizado por compreender:

(a) prover uma pluralidade de fitas de polímero estirado, alinhadas de tal modo que cada fita é orientada em paralelo às fitas adjacentes, e pelo que as fitas adjacentes não se sobrepõem;

5 (b) posicionar as várias fitas de polímero estirado sobre um substrato móvel desse modo formando uma primeira monocamada;

(c) segurar a primeira monocamada sobre o substrato móvel;

10 (d) posicionar uma pluralidade de fitas de polímero estirado sobre a primeira monocamada, desse modo formando uma segunda monocamada, onde a direção da segunda monocamada faz um ângulo  $\alpha$  com relação à primeira monocamada; e

15 (e) comprimir a pilha assim formada para consolidar as suas monocamadas.

18. Processo, de acordo com a reivindicação 17, caracterizado pelo fato de que a etapa (a) compreende ainda a etapa de aplicar um aglutinante ou um meio e aglutinação 20 às fitas adjacentes.

19. Processo, de acordo com a reivindicação 17 ou 18, caracterizado pelo fato de que as várias fitas de polímero estirado são desenroladas de uma estação de desenrolamento e a etapa (d) é realizada mediante dobradura das várias 25 fitas de polímero estirado ao menos parcialmente sobre elas próprias.

20. Processo, de acordo com a reivindicação 17, 18 ou 19, caracterizado pelo fato de que as várias fitas de polímero estirado são posicionadas de tal modo que a 30 primeira monocamada forma um ângulo  $\beta$  com relação à direção

de movimento do substrato, e a dobradura é realizada de tal modo que a linha de dobra se estende aproximadamente paralela à direção de movimento do substrato.

21. Processo, de acordo com a reivindicação 20,  
5 caracterizado pelo fato de que o ângulo β está entre 40 e 50 graus.

22. Processo, de acordo com qualquer uma das reivindicações 17, 18, 19, 20 ou 21, caracterizado pelo fato de que a segunda monocamada é ao menos parcialmente  
10 aderida à primeira monocamada.

23. Processo para fabricação de um artigo de resistência balística, caracterizado por compreender:

(a) empilhar ao menos duas monocamadas de polímero estirado unidirecionais, por meio das quais difere a 15 direção de tiragem de 2 monocamadas subseqüentes na pilha, onde ao menos uma monocamada compreende uma pluralidade de fitas unidirecionais do polímero estirado, alinhadas na mesma direção, por meio das quais fitas adjacentes não se sobrepõem, e uma folha de material selecionada do grupo 20 consistindo em cerâmica, aço, alumínio, titânio, vidro e grafite, ou suas combinações; e

(b) consolidar as folhas empilhadas sob temperatura e pressão.

24. Artigo de resistência balística, caracterizado por  
25 compreender uma folha de material de múltiplas camadas de acordo com qualquer uma das reivindicações 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15 ou 16.

25. Artigo de resistência balística, de acordo com a reivindicação 24, caracterizado por compreender ao menos 40  
30 monocamadas unidirecionais.

26. Artigo de resistência balística, de acordo com a reivindicação 24 ou 25, caracterizado por compreender uma folha adicional de material inorgânico selecionado do grupo consistindo em cerâmica, aço, alumínio, magnésio-titânio, 5 níquel, cromo e ferro ou suas ligas, vidro e grafite, ou combinações dos mesmos.

27. Artigo de resistência balística, de acordo com a reivindicação 26, caracterizado pelo fato de que a folha adicional de material inorgânico é posicionada do lado 10 externo da pilha de monocamadas ao menos na sua face de impacto.

28. Artigo de resistência balística, de acordo com a reivindicação 26 ou 27, caracterizado pelo fato de que a espessura da folha adicional de material inorgânico é de no 15 máximo 50 mm.

29. Artigo de resistência balística, de acordo com qualquer uma das reivindicações 26, 27 ou 28, caracterizado pelo fato de que uma camada de ligação está presente entre a folha adicional de material inorgânico e a folha de 20 material de acordo com qualquer uma das reivindicações 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15 ou 16, a camada de ligação compreendendo uma camada tecida ou não-tecida de fibra inorgânica.

30. Processo para preparação de uma folha de material de múltiplas camadas, de acordo com qualquer uma das reivindicações 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15 ou 16, caracterizado por compreender:

(a) posicionar ao menos uma primeira fita unidirecional de polímero estirado sobre um substrato móvel 30 desse modo formando uma primeira monocamada, pelo que a

monocamada é livre de uma área de espessura elevada adjacente e ao longo do comprimento substancial das bordas longitudinais da ao menos uma fita unidirecional;

5 (b) segurar a primeira monocamada sobre o substrato móvel;

(c) ao menos uma segunda fita unidirecional de polímero estirado sobre a primeira monocamada, desse modo formando uma segunda monocamada, pelo que a direção da segunda monocamada faz um ângulo α com relação à primeira 10 monocamada; e

(d) comprimir a pilha assim formada para consolidar as suas monocamadas.

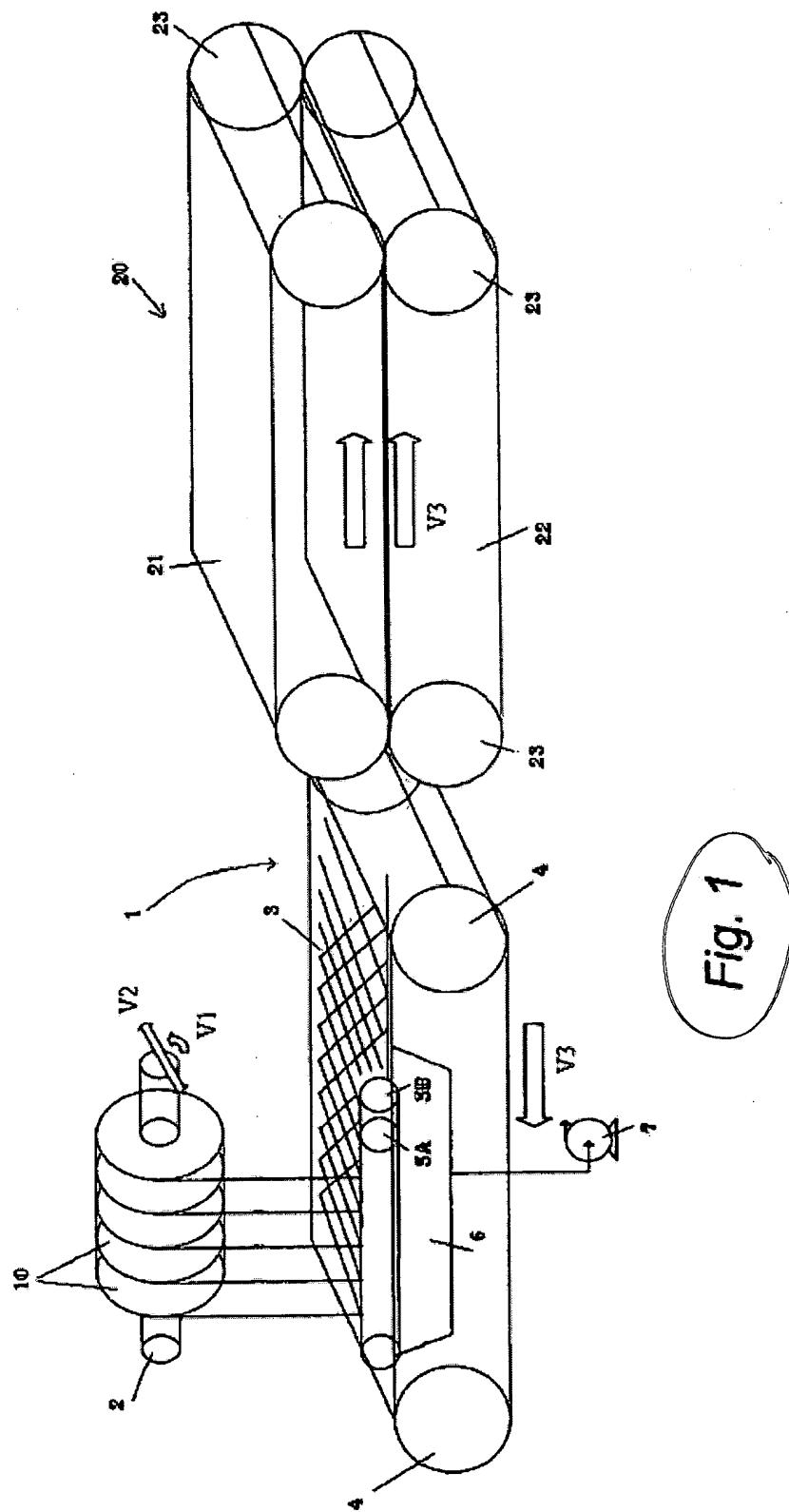
31. Processo para a fabricação de um artigo de resistência balística caracterizado por compreender:

15 (a) empilhar ao menos duas monocamadas de polímero estirado unidireccionais, cada monocamada compreendendo ao menos uma fita unidirecional, por meio da qual difere a direção de tiragem de 2 monocamadas subsequentes na pilha, pelo que ao menos uma monocamada é livre de uma área de 20 espessura elevada adjacente e ao longo do comprimento substancial das bordas longitudinais da ao menos uma fita unidirecional; e uma folha de material selecionada do grupo consistindo em cerâmica, aço, alumínio, titânio, vidro e grafite, ou combinações dos mesmos; e

25 (b) consolidar as folhas empilhadas sob temperatura e pressão.

32. Folha de material de múltiplas camadas, de acordo com qualquer uma das reivindicações 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15 ou 16, caracterizada pelo fato de 30 que ao menos uma monocamada compreende uma pluralidade de

fitas unidireccionais do polímero estirado, alinhadas de tal modo que as várias fitas unidireccionais formam um tecido trançado.



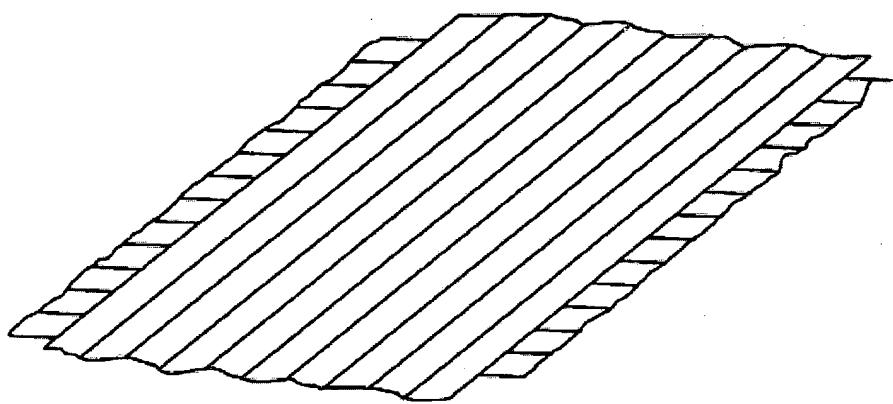


Fig. 2

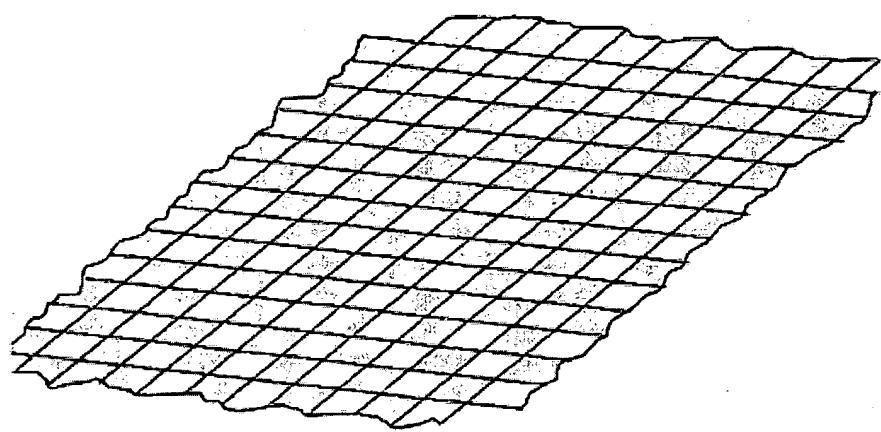


Fig. 3

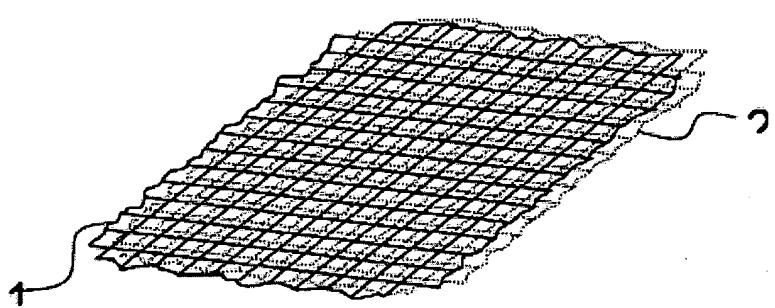


Fig. 4

FOLHA DE MATERIAL DE MÚLTIPLAS CAMADAS E PROCESSO PARA SUA  
PREPARAÇÃO

A invenção se refere a uma folha de material de múltiplas camadas compreendendo uma pilha consolidada de monocamadas unidirecionais de polímero estirado, pelo que difere a direção de estiramento de duas monocamadas subsequentes na pilha. Ao menos uma monocamada compreende uma pluralidade de fitas unidirecionais do polímero estirado, alinhadas na mesma direção, pelo que fitas adjacentes não se sobrepõem. A invenção também se refere a um processo para a preparação da folha de material de múltiplas camadas, e a um artigo de resistência balística compreendo a folha de material de múltiplas camadas.



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(54) **METHOD TO PRODUCE BALLISTIC AND STAB RESISTANT STRUCTURES FOR GARMENTS AND STRUCTURES PRODUCED BY THE METHOD**

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#### **ABSTRACT**

The invention pertains to a composite wherein the composite comprises at least one fabric and a thermoplastic polymeric resin wherein the resin is impregnated into the fabric to an extent that between 80 to 95% of the maximum volumic mass (void volume) of the fabric is filled with resin. The fabric and thermoplastic resin are combined with one or two release layers to form an assembly. A plurality of these assemblies is combined to form a stack which is subjected to thermopressing wherein the thermopressing is carried out in at least two cycles with a pressure release between each cycle.

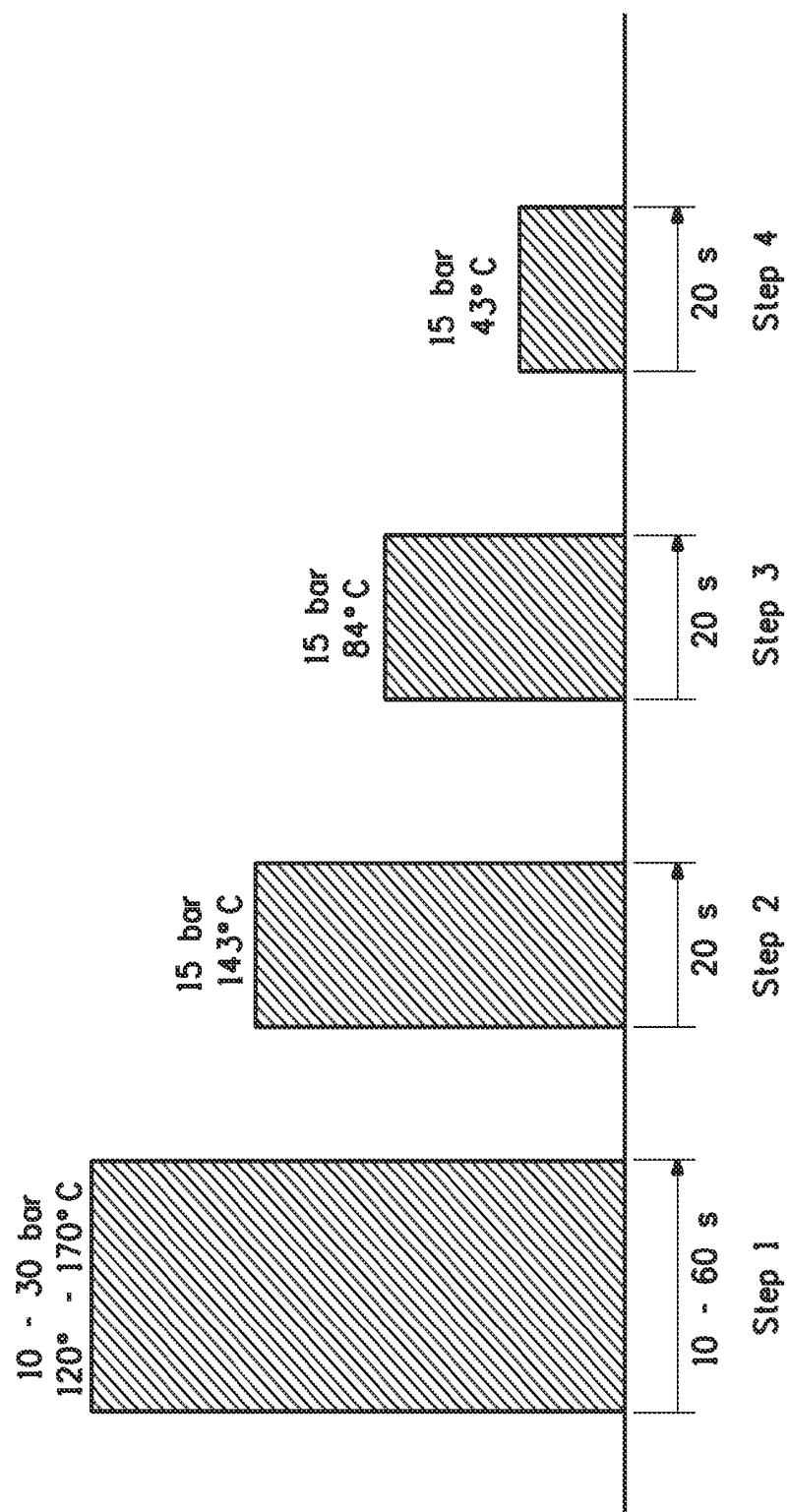


FIG. 1

## METHOD TO PRODUCE BALLISTIC AND STAB RESISTANT STRUCTURES FOR GARMENTS AND STRUCTURES PRODUCED BY THE METHOD

### BACKGROUND

[0001] 1. Field of the Invention

[0002] The present invention relates to enhanced, flexible light weight energy absorbing materials and methods of making them. These materials have utility in the manufacture of personal protection equipment, such as soft armor, stab, spike and hypodermic needle protection systems.

[0003] 2. Description of Related Art

[0004] Aramid fibers are a class of heat-resistant and strong synthetic fibers that are used in a wide variety of industrial applications. One prominent use of aramid fibers is in ballistic rated body armor fabrics, such as personal protection equipment (PPE), such as bullet-resistant vests.

[0005] While the woven aramid fabrics in PPE offer good protection against ballistic threats such as bullets, they are more vulnerable to sharp and thin weapons such as knives and ice picks. This is can be explained by the fact that thin weapons can pass between the fibers making up the fabric, because the fibers are pushed apart by the penetrating point of the weapon. In an effort to improve the protection against knife and spike attacks, protective fabrics are now commonly reinforced with synthetic resins that can be of thermoplastic or thermoset nature, and which restrict relative movement of the fibers in the case of an attack. Thus, the fibers cannot be pushed apart by a thin weapon because they are partially or fully fixed in place by the resin. Such a technology is described in, for example, WO 2001/037691 which discloses a protective material that is more flexible than other known protective materials and where the gain in flexibility is primarily achieved by the low denier count of the fibers used. The fibers are furthermore embedded within a support material to restrict relative movement of the fibers and thus to achieve good protection against knife or needle attacks.

[0006] However, when embedding the fibers of a protective material such as for example para-aramid fabrics with polymeric resins, there is always also a rigidification that is caused by the embedding, because the embedding reduces the ability of the fibers to move relative to each other. For example, when an embedded fabric is bent, it will immediately snap back into its initial shape, in contrast to a non-embedded fabric. Therefore, embedded fabrics are stiffer when compared to non-embedded fabrics and concurrently, personal protection equipment (PPE) manufactured from embedded fabrics are perceived as causing more discomfort. This perception leads to a reduced willingness to wear the PPE and therefore needs to be prevented by offering a more supple and/or flexible PPE.

[0007] Embedding of the fibers is commonly carried out in known manners, such as for example by lamination, calendering or heat pressing of thermoplastic or thermoset resin sheets onto the fibers. As the necessary machinery is well known and used by many manufacturers of personal protection equipment (PPE), it is desirable to reduce the modification of the embedding methods to a minimum so that eventual new resins can be applied in the same known fashion.

[0008] U.S. Pat. No. 5,866,658 discloses thermoplastic compositions which are blends of ionomers with polyamides. However, the blends are used as molded parts for automotive applications such as bumpers, fender extensions and hub caps, to improve high gloss, toughness and scratch resistance.

[0009] U.S. Pat. No. 5,859,137 discloses thermoplastic ionomers based on copolymers of ethylene and carboxylic acids as well as combinations of such ionomers with polyamides. However, such combinations are mainly useful for applications to improve impact resistance and mechanical strength.

[0010] PCT publication WO 01/37691 discloses a protective material comprising a plurality of separate flexible layers each layer comprising a plurality of high strength fibers capable of resisting penetration by a knife or sharp-pointed objects such as icepicks and hypodermic needles, and a support material, wherein at least part of the fibers are embedded within the support material to restrict relative movement of the fibers therein. The high-strength fibers are of equal below 600 deniers.

[0011] PCT publication WO 03/053676 discloses multiple threat penetration resistant articles. The articles include, fabric layers, polymer impregnated fabric layers and woven fabric layers. The articles can additionally include tightly woven fabric layers which define the strike face of the article.

[0012] PCT publication WO 2011/156577 discloses enhanced flexible lightweight ballistic, stab and spike resistant materials which use a thermoplastic composition for manufacturing personal protection equipment, wherein the thermoplastic composition comprises at least a first thermoplastic polymer that has a melting point different to the melting point of a second thermoplastic polymer.

[0013] PCT publication WO 2010/036406 discloses a method for producing fiber composites impregnated with a thermoplastic resin to be used as stab and ballistic composite structures.

[0014] PCT publication WO2008/105929 relates to adhesive compositions used in composite laminar structures to improve ballistic resistance, for example, which limits the penetration of a bullet from a gun. The composite laminar structures includes composite laminar structure, includes an aramid or olefin fiber layer, a eutectic impact absorbing adhesive resin or adhesive composition layer, and an ionomer layer. The aramid or olefin fiber layer is adhesively bonded with the eutectic impact absorbing adhesive resin or adhesive composition layer to the ionomer layer. In further embodiments, the composite laminar structure includes an olefin fiber layer, a eutectic amorphous acid functional polypropylene copolymer adhesive layer, and an ionomer layer. The olefin fiber layer is adhesively bonded with the eutectic amorphous acid functional polypropylene copolymer adhesive layer to the ionomer layer. The olefin fiber layer has no polarity within a matrix thereof and has no affinity for moisture.

[0015] PCT publication WO2006/069950 relates to a heat-shrinkable multilayered film comprising at least one carrier layer a) based on at least one thermoplastic polymer, at least one gas barrier layer, and at least one sealing layer. The entire free surface of the carrier layer opposing the gas barrier layer is covered with an outer release layer having a plasticizing or melting temperature that is at least 30° C. higher than the sealing or melting temperature of the sealing layer.

[0016] U.S. Pat. No. 6,645,336 to Albertone describes a process for the preparation of a laminate, particularly a waterproof moisture vapor permeable laminate, comprising a substrate having on a surface thereof a thermoplastic polymer resin coating and further comprising a peelable release layer in contact with the surface of the thermoplastic polymer resin remote from the substrate, and optionally further comprising a tie layer between the substrate and the thermoplastic poly-

mer resin, the process comprising the steps of forming or providing a substrate layer and providing on a surface thereof a thermoplastic polymer resin coating and a peelable release layer and optionally providing a tie layer between the substrate and the thermoplastic polymer resin coating, characterized in that the thermoplastic polymer resin has a viscosity less than about 3000 Pa·s measured according to the standard ISO11443.

[0017] PCT publication WO 2002/26463 discloses an efficient method of simultaneously molding multiple composite laminates comprising layering one or more layers of wet-laid, non-woven mats comprised of particulate thermoplastic polymer and a fiber reinforcement between one or more layers of a release film material and molding the combination to form multiple laminates.

[0018] With the aim of further improving stab and ballistic resistance of protective articles, composite structures based on resins and aramid fabrics have been developed such as WO 2001/037691 cited above. It discloses a protective material comprising a plurality of separate flexible layers, each layer comprising a plurality of high-strength fibers and a support material made of a resin. By being embedded within the resin, the relative movement of the fibers upon an impact caused to the wearer is reduced thus leading to an increased blunt trauma resistance.

[0019] Conventional processes used to manufacture such composite materials involve first a lamination step and then a resin melting step. The lamination step comprises the extrusion of the resin into a film, which film is then laminated onto the fabric made of high-strength fibers in order to have a sufficient adhesion between the film and the fabric and to form a composite assembly. This process requires the use of a release layer which is typically made of silicone paper and which is positioned between the film and the laminating rolls to prevent the so-manufactured composite assembly from sticking to the heated rolls. The use of these release layers requires manufacturing machines with three or more rolls depending on whether the fabric is impregnated on one side or both sides. This implies more complex tensioning systems and operating procedures and lowers the overall manufacturing speed.

[0020] In the resin flowing step, the composite assembly obtained under the lamination step undergoes heat and pressure in a heating press (thermopressing) in order to allow the resin to flow through the fabric and, therefore, to at least partially impregnate it. The resin impregnation improves the protective effect of the final composite structure. The flowing step is typically a batch process where sheets of composite assembly manufactured under the lamination step are pressed together.

[0021] In order to increase the production yield under the resin flowing step, it is known to load the heating press with as many layers as possible of the composite assembly obtained under the lamination step. In such a case it is however essential to interpose a release layer like that described above between each of two composite assembly layers in order to prevent them from fusing together during thermopressing. The preparation of this multilayer stack is made by a conventional machine which alternatively deposits release layers and composite assemblies, and optionally cuts the borders of the stack to match the size of the heating press. After pressing and cooling the stack, the release layers between each so impregnated composite structure must be eventually removed.

[0022] The use of release layers during the lamination step and the resin flowing step increases the complexity and costs of the overall manufacturing process. Moreover, the release material described above is expensive and cannot be used for more than a production cycle and it is usually difficult to dispose of, particularly if made of silicone paper. An increase of energy consumption associated with the thickness of the silicone paper further strengthens the environmental concerns.

[0023] There is however a need to further reduce the rigidity of embedded fabrics for example as disclosed in WO 2011/156577, while at the same time offering comparable protection against multiple threats such as knife, stab and needle attacks and also at the same time provide a solution that can be executed on pre-existing machinery in an efficient production process with an improved productivity as a new and inventive improvement over the method disclosed in WO 2010/036406.

## SUMMARY OF THE INVENTION

[0024] This invention pertains to a method of producing composite comprising the steps of:

[0025] (a) providing an assembly comprising in order, a release layer, a thermoplastic resin layer, a fabric and, optionally, a second release layer,

[0026] (b) combining a plurality of assemblies of step (a) into a stack,

[0027] (c) Subjecting the stack from step (b) to a thermopressing process wherein the process comprises a minimum of two cycles where each cycle comprises

[0028] (i) thermopressing the stack for a defined period under a defined temperature and pressure, and

[0029] (ii) releasing the pressure on the stack for a defined period of time,

[0030] (d) cooling the stack,

[0031] (e) removing the individual assemblies from the stack, and

[0032] (f) removing the release layer(s) from each assembly to leave a composite,

wherein the defined time periods, temperatures and pressures of each thermopressing cycle are such that the composite has between 80 to 95% of the void volume of the fabric filled with resin.

[0033] The invention further pertains to a ballistic, knife and pick resistant article comprising a plurality of composites made by the above method wherein the composite comprises at least one fabric and a thermoplastic polymeric resin wherein the resin is impregnated into the fabric to an extent that between 80 to 95% of the maximum volumic mass (void volume) of the fabric is filled with resin.

## BRIEF DESCRIPTION OF THE DRAWINGS

[0034] FIG. 1 shows one example of a thermopressing cycle.

## DETAILED DESCRIPTION

[0035] The present invention solves the problems stated in the background section by providing a fabric-thermoplastic resin composite for the use in personal protection equipment (PPE), wherein the thermoplastic composition is embedded in the fiber in order to form non-continuous continuum with the fibers and across the fibrous layer section. The term melting point as used in this description is intended to mean the

temperature determined by means of DSC (Differential Scanning calorimetry) at heating rates of 10 degrees C. per minute, according to DIN 53765-8-10. The term non-continuous continuum with the fibers as used in this description refers to an interrupted three-dimensional matrix where some places are not restricted for relative movement of the fibers with the polymer matrix.

### Composite

[0036] The composite of this invention comprises at least one fabric and a thermoplastic polymeric resin wherein the resin is impregnated into the fabric to an extent between 80 to 95% of the maximal volumic mass. The maximal volumic mass corresponds to a total impregnation of the fabric with the polymer. Maximal volumic mass can be defined by the density obtained after pressing the fabric with the polymer at a temperature of about 60° C. above the polymer melting temperature and at a pressure of 20 bars for 30 minutes.

[0037] Voids are any free spaces in the fiber resin matrix that are not fiber or resin. If the void volume of fabric is filled with resin to an extend such as the volumic mass is greater than 95% of the maximal volumic mass then the resulting composite is too stiff and will not have a bending stiffness lower than 300 mNm. If the void volume of fabric is insufficiently filled with resin, that is, to an amount of less than 80% of the maximal volumic mass, then the ability of an article comprising a plurality of composites to prevent knife or spike penetration is compromised.

### Thermoplastic Resin

[0038] The thermoplastic polymer according to the present invention may be polyvinyl, polyolefin and/or polycondensates such as polyethylene, polyethylene copolymers, polypropylene, polypropylene copolymers, polybutylene, polybutylene copolymers, polyamides, polyamide copolymers, polyesters, polyurethanes, polyurethane copolymers, polyacrylonitriles, polysulfones, thermoplastic silicone copolymers, thermoplastic elastomeric block copolymers, such as acrylonitrile-butadiene-styrene, polyisopropene-polyethylene-butylene-polystyrene or polystyrene-polyisoprene-polystyrene block copolymers, polyether-ester block copolymers, and/or combinations thereof. Preferably, the thermoplastic polymer is chosen among those mentioned polymers having a melting point in the range of from 60° C. to 250° C. and more preferably from 60° C. to 150° C.

[0039] Preferably, the thermoplastic polymer according to the present invention can be chosen among polymers, for example, thermoplastic elastomeric block copolymers, like for example, but not limited to, polyisopropene-polyethylene-butylene-polystyrene or polystyrene-polyisoprene-polystyrene block copolymers, or, for example, polyolefins, like for example, but not limited to, polyethylenes, for example, low density polyethylenes, very low density polyethylenes, metallocene polyethylenes and/or polyethylene copolymers, for example, ethylene/α,β-unsaturated-C3-C8 carboxylic acid copolymers and/or ethylene/α,β-unsaturated-C3-C8 carboxylic acid copolymers partially neutralized with metal salts.

[0040] More preferably, the thermoplastic polymer according to the present invention can be chosen among polyethylene copolymers, for example, ethylene/α,β-unsaturated

C3-C8 carboxylic acid copolymers and/or ethylene/α,β-unsaturated C3-C8 carboxylic acid copolymers partially neutralized with metal salts.

[0041] In the case where the thermoplastic polymer is an ethylene/α,β-unsaturated C3-C8 carboxylic acid copolymer, the α,β unsaturated C3-C8 carboxylic acid can be chosen from acrylic acid and/or methacrylic acid.

[0042] The ethylene/α,β-unsaturated C3-C8 carboxylic acid copolymer is preferably a terpolymer of ethylene, α,β-unsaturated C3-C8 carboxylic acid and α,β-unsaturated C3-C8 dicarboxylic acid.

[0043] The α,β-unsaturated C3-C8 dicarboxylic acid can be chosen from maleic acid, maleic anhydride, C1-C4 alkyl half esters of maleic acid, fumaric acid, itaconic acid and itaconic anhydride.

[0044] Preferably, the α,β unsaturated C3-C8 dicarboxylic acid can be chosen from maleic anhydride, ethyl hydrogen maleate and methyl hydrogen maleate.

[0045] Most preferably, the α,β-unsaturated C3-C8 dicarboxylic acid is maleic anhydride, methyl hydrogen maleate and/or combinations thereof.

[0046] The ethylene/α,β-unsaturated C3-C8 carboxylic acid/α,β-unsaturated C3-C8 dicarboxylic acid polymer can further comprise up to 40 weight percent of an C1-C8 alkyl acrylate softening comonomer, which is preferably chosen among methyl(meth)acrylate, ethyl(meth)acrylate or n-butyl (meth)acrylate, more preferably from n-butyl acrylate or ethyl(meth)acrylate.

[0047] The term softening comonomer as mentioned in this description is well-known to those skilled in the art and refers to comonomers such as the C1-C8 alkyl acrylate mentioned above.

[0048] The term (meth)acrylate as mentioned in this description is respectively intended to mean acrylate and methacrylate.

[0049] In the ethylene/α,β-unsaturated C3-C8 carboxylic acid/α,β-unsaturated C3-C8 dicarboxylic acid polymer, the α,β-unsaturated C3-C8 carboxylic acid can be present in a range of 2 to 25 weight percent and the α,β-unsaturated C3-C8 dicarboxylic acid can be present in a range of 0.1 to 15 weight percent with the proviso that the α,β-unsaturated C3-C8 carboxylic acid and the α,β-unsaturated C3-C8 dicarboxylic acid are present from 4 to 26 weight percent, and with the further proviso that the total comonomer content, including the C1-C8 alkyl acrylate softening comonomer, does not exceed 50 weight percent.

[0050] Most preferably, the thermoplastic polymer according to the present invention is an ethylene/α,β-unsaturated C3-C8 carboxylic acid copolymer partially neutralized with metal ions, which is commonly referred to as "ionomer". The total percent neutralization is from 5 to 90 percent, preferably 10 to 70 percent, most preferably between 25 and 60 percent of the ionomer.

[0051] In the case where the thermoplastic polymer is an ethylene/α,β-unsaturated C3-C8 carboxylic acid copolymer partially neutralized with metal ions, the α,β-unsaturated C3-C8 carboxylic acid can be chosen from acrylic acid and/or methacrylic acid.

[0052] The ethylene/α,β-unsaturated C3-C8 carboxylic acid copolymer partially neutralized with metal ions is preferably a terpolymer of ethylene, α,β-unsaturated C3-C8 carboxylic acid and α,β-unsaturated C3-C8 dicarboxylic acid partially neutralized with metal ions.

[0053] The  $\alpha,\beta$ -unsaturated C3-C8 dicarboxylic acid can be chosen from the same components as already described above.

[0054] The ethylene/ $\alpha,\beta$ -unsaturated C3-C8 carboxylic acid/ $\alpha,\beta$ -unsaturated C3-C8 dicarboxylic acid polymer partially neutralized with metal ions can further comprise up to 40 weight percent of an C1-C8 alkyl acrylate softening comonomer, which is preferably chosen among the same components as already described above.

[0055] In the ethylene/ $\alpha,\beta$ -unsaturated C3-C8 carboxylic acid/ $\alpha,\beta$ -unsaturated C3-C8 dicarboxylic acid polymer partially neutralized with metal ions, from 5 to 90 percent of the total number of  $\alpha,\beta$ -unsaturated C3-C8 carboxylic acid units in the polymer are neutralized with metal ions, and the  $\alpha,\beta$ -unsaturated C3-C8 carboxylic acid and the  $\alpha,\beta$ -unsaturated C3-C8 dicarboxylic acid can be present in the same amounts as described above, with the same proviso regarding the  $\alpha,\beta$ -unsaturated C3-C8 carboxylic acid and the  $\alpha,\beta$ -unsaturated C3-C8 dicarboxylic acid and the same further proviso regarding the total comonomer content, including the C1-C8 alkyl acrylate softening comonomer, as described above.

[0056] The ethylene/ $\alpha,\beta$ -unsaturated C3-C8 carboxylic acid copolymer that are partially neutralized are partially neutralized with metal ions which can be any metal ion of group I or group II of the periodic table. In practice however, the preferred metal ions are sodium, zinc, lithium, magnesium, calcium or a mixture of any of these. More preferred are sodium, zinc, lithium and magnesium. Most preferably, the ion is zinc, lithium and/or combinations thereof.

[0057] The partially neutralized ethylene/ $\alpha,\beta$ -unsaturated C3-C8 carboxylic acid copolymers according to the present invention may be prepared by standard neutralization techniques, as disclosed in U.S. Pat. No. 3,264,272.

[0058] The resulting ionomers may have an melt index (MI) of from 0.01 to 100 grams/10 minutes, preferably 0.1 to 30 grams/10 minutes, as measured using ASTM D-1238, condition E (190° C., 2160 gram weight).

[0059] The above ionomers can be prepared by free-radical copolymerization methods, using high pressure, operating in a continuous manner known in the art such as is described in U.S. Pat. Nos. 4,351,931; 5,028,674; 5,057,593 and 5,859,137.

[0060] The successful use of the thermoplastic composition according to the present invention relies mainly on the fact that the thermoplastic polymer is dispersed in a non-continuous continuum.

[0061] In addition, the thermoplastic composition may optionally comprise reactive or non-reactive additives such as, but not limited to, colorants, diluents, processing agents, UV additives, fire retardants, mineral fillers, organic fillers, bonding additives, surfactants, aramid pulp, antioxidants, antistatic, slip agents, tackifiers, plasticisers, and/or combinations thereof as known in the art and which can be incorporated by known methods.

[0062] Fire retardants may be chosen from brominated flame retardants, red phosphorus, asbestos, antimony trioxide, borates, metal hydrates, metal hydroxides, Tetrakis(hydroxymethyl)phosphonium salts, fluorocarbons and/or combination thereof.

#### Fabric

[0063] Suitable fabrics are those comprising fibrous yarns having a yarn tenacity of at least 15 g/dtex, and a tensile modulus of at least 40 g/dtex. Preferably, the yarns have a

tenacity of at least 20 g/dtex, and a tensile modulus of at least 500 g/dtex. In some embodiments, the yarns have a linear density of from 220 to 3300 dtex or even from 440 to 1400 dtex. In another embodiment, the yarns have a linear density of 1100 dtex.

[0064] The ballistic resistant fabric of this invention may be a woven fabric, a knit, a unidirectional fabric, a multiaxial fabric, a nonwoven fabric, a three-dimensional (3D) fabric or a combination thereof. A woven fabric, a unidirectional fabric and a multiaxial fabric comprise yarns of continuous filaments. A multiaxial fabric may also comprise a nonwoven fabric. In the context of this invention, a nonwoven fabric is a fabric comprising randomly oriented short fibers. Examples of a nonwoven fabrics are a needled or hydroentangled felts, meltblown and/or spunbonded fabrics. Examples of woven fabrics are plain weaves, satin weaves, crowfoot weaves, rip-stop weaves, basket weaves, leno weaves and twill weaves.

[0065] A unidirectional fabric is a fabric wherein all the yarns within one layer of the fabric are aligned in one direction. A multiaxial fabric is a non-crimped fabric comprising a plurality of unidirectional fabric layers wherein the yarn orientation between successive layers is in a different direction. Common multiaxial fabrics comprise two, four or six layers. U.S. Pat. No. 6,000,055 to Citterio describes a multiaxial layer suitable for use in a ballistic resistant article.

[0066] Pluralities of adjacent unidirectional fabric layers are held together by stitching in a transverse direction through the plane of the unidirectional layers or from a polymeric bonding substrate placed between the adjacent layers. In some embodiments, a combination of both transverse yarn stitching and a polymeric bonding substrate may be used.

[0067] All the above fabric types are well known in the textile art.

[0068] The fiber material of the fabric can be chosen among aromatic polyamide fibers, such as for example, but not limited to, poly-paraphenylene terephthalamide (p-aramid) commercially available as Kevlar® from E.I. du Pont de Nemours and company, Wilmington, Del. (hereinafter DuPont), poly-metaphenylene terephthalamide (m-aramid) commercially available as Nomex® also from DuPont and, liquid crystalline polymer and ladder-like polymer fibers, for example, polybenzimidazoles or polybenzoxazoles, especially poly-para-phenylene-2,6-benzobisoxazole (PBO), 5-amino-2-(p-aminophenyl)-benzimidazole, or poly(2,6-diimidazo[4,5-b:4,5-c]pyridinylene-1,4-(2,5-dihydroxyl)phenylene) fibers, highly oriented polyolefin fibers, for example, high molecular weight polyethylene (HMPE) fibers, polypropylene fibers, ballistic nylons, high strength mineral fibers, for example, glass fibers, basalt fibers and/or combinations thereof, provided that the ballistic fabric meets the ballistic performance requirements, as known to those skilled in the art.

[0069] Preferably, the fiber material can be chosen among highly oriented polyolefin fibers, aromatic polyamide fibers, PBO fibers, or glass fibers, and/or combinations thereof. More preferably, the fiber material is poly-paraphenylene terephthalamide or poly-metaphenylene terephthalamide. A preferred aromatic polyamide is para-aramid. As used herein, the term para-aramid filaments means filaments made of para-aramid polymer. The term aramid means a polyamide wherein at least 85% of the amide ( $-\text{CONH}-$ ) linkages are attached directly to two aromatic rings. Suitable aramid fibers are described in Man-Made Fibers—Science and Technology, Volume 2, in the section titled Fiber-Forming Aromatic

Polyamides, page 297, W. Black et al., Interscience Publishers, 1968. Aramid fibers and their production are, also, disclosed in U.S. Pat. Nos. 3,767,756; 4,172,938; 3,869,429; 3,869,430; 3,819,587; 3,673,143; 3,354,127; and 3,094,511.

[0070] An advantage of using the thermoplastic composition according to the present invention in PPE is that the shelf life is almost unlimited for fabrics pre-impregnated with the thermoplastic polymer, in contrast to fabrics pre-impregnated with curable thermoset resins widely used in the art of ballistic protection systems, which have a limited shelf life. Fabrics pre-impregnated with curable thermoset resins slowly cure even when stored at cool temperatures, which is why they need to be processed quickly after pre-impregnation. In addition, thermoset resins heavily used in the field, such as phenolic resins, liberate VOCs (Volatile Organic Compounds) and require additional venting of the storage spaces and additional safety measures during processing.

[0071] Also, curable materials such as epoxy resins or phenolic resins are much more rigid than the thermoplastic compositions according to the present invention, which adds to the discomfort felt by the wearer. Without wishing to be held to particular theory, the non-continuous voids are acting as a softening agent by interrupting the otherwise continuous phase of thermoplastic polymer. Instead of embedding the fibers with a continuous thermoplastic polymer, the process according to the present invention will create interruptions in the otherwise homogenous composite structure. This creates a network-like phase of voids which will not therefore contact the entirety of the fiber surface, which results in unexpected benefit of increased flexibility of the reinforced fabric layer according to the present invention. Partial but continuous and uniform impregnation across the layer section will occur and surprisingly favour the flexing ability of the layers and resulting pack assemblies. The present invention further provides for a ballistic fabric that is reinforced with a thermoplastic resin, which can be particularly useful in manufacturing thermoformed personal protection equipment suited for the female anatomy.

[0072] The thickness of the thermoplastic resin layer prior to impregnation into the fabric may be chosen depending on the end-use application. The optimal thickness of the thermoplastic layer depends on the number and thickness of fabrics that must be impregnated with the thermoplastic resin. If only one side of the fabric layer(s) has to be impregnated, then the thickness of the at least one thermoplastic layer is preferably from 10 to 200 µm. If both sides of the fabric layer(s) have to be impregnated, then the thickness of each at least one thermoplastic layer should preferably be from 5 to 150 micrometers and more preferably from 15 to 100 micrometers. A primary reason for this preferred difference in thickness of the at least one thermoplastic layer is that sufficient thermoplastic resin should be available for proper impregnation of the aramid fabric layer in order to form an interpenetrating network of fibers substantially surrounded by the thermoplastic resin. In the composite the thermoplastic layer has been impregnated into the fabric layer and is no longer present in the form of a distinct layer, but rather as a thermoplastic resin continuum on the surface of and within the fabric layer.

[0073] According to the present invention, the fabric is reinforced with a thermoplastic composition.

#### Protective Article

[0074] A plurality of composites of this invention can be assembled into a protective article. The article may comprise

other components such as foam, metal, glass or ceramics. Preferably, the individual composites of the article according to the invention are not connected to each other in a way that restricts their movement relative to each other, but only in a way to form a stack comprising a coherent bundle of free individual composites. This can be done, for example, by stitching the assembly of composites in such a way that only a very small percentage, say less than 10% or 5%, of the surfaces of the composites are stitched together. This can be done, for example, by edge or corner stitching, these techniques being well known in the art. Alternatively, the fabric layers may be stacked on top of each other and placed into pouches or bags. Thus each individual reinforced fabric layer of the invention is able to move with respect to other fabric layers, within the plane defined by that individual reinforced fabric layer. Alternatively, the stack can be taped along the edges.

[0075] The article may be useful in different applications where protection is sought against multiple threats, such as for example knife and spike threats, but also against ballistic threats, in garments or articles such as for example, ballistic rated body armor.

Method of Making the Composite A method of making the composite comprises the steps of:

[0076] (a) providing an assembly comprising in order, a release layer, a thermoplastic resin layer, a fabric and, optionally, a second release layer,

[0077] (b) combining a plurality of assemblies of step (a) into a stack,

[0078] (c) subjecting the stack from step (b) to a thermopressing process wherein the process comprises a minimum of two cycles where each cycle comprises

[0079] (i) thermopressing the stack for a defined period under a defined temperature and pressure, and

[0080] (ii) releasing the pressure on the stack for a defined period of time,

[0081] (d) cooling the stack,

[0082] (e) removing the individual assemblies from the stack, and

[0083] (f) removing the release layer(s) from each assembly to leave a composite,

[0084] wherein the defined time periods, temperatures and pressures of each thermopressing cycle are such that the composite has between 80 to 95% of the void volume of the fabric filled with resin.

[0085] The composite can be made by applying the thermoplastic composition to the fabric using methods known in the art, such as, but not limited to, lamination, calendaring, heat pressing, powder impregnation, liquid impregnation, extrusion coating, and/or combinations thereof. Preferably, the reinforcement of the fabric is achieved by thermopressing with the thermoplastic composition.

[0086] The thermoplastic composition can be applied in various forms such as, but not limited to, sheets, fabrics, hotmelts, powder, liquids, and/or combinations thereof. Preferably, the thermoplastic resin is applied as a sheet having a thickness of 10 to 200 micrometers. More preferably, the thermoplastic resin is applied as a sheet having a thickness of 30 to 150 micrometers. Most preferably, the thermoplastic composition is applied as a sheet having a thickness of 40 to 100 micrometers.

[0087] The temperature at which the fabric is reinforced with the thermoplastic composition must be at least at or above the melting point of the thermoplastic polymer, with

the proviso that the temperature at which the fabric is reinforced with the thermoplastic composition does not exceed a temperature that adversely affects the fabric fiber. These temperatures are, for example, at 230° C. for aramids, 140° C. for high molecular weight polyethylene (HMPE), 300° C. for PBO and 450° C. for glass fiber.

[0088] In some embodiments, the resin and release layer may be pre-combined by lamination or extrusion or they may be co-extruded.

[0089] The release layer is prepared by conventional methods such as for example blown film extrusion, cast film extrusion or cast sheet extrusion. Preferably the release layer has a melting temperature which is substantially higher than that of the thermoplastic resin layer in order for the release layer to remain physically and chemically intact during subsequent processing and to be eventually easily peeled off from the impregnated fabric layer. Preferably the melting temperature of the release layer is at least 20° C., still more preferably at least 50° C., higher than the melting temperature of the thermoplastic layer.

[0090] Examples of polymers suitable for use as a release layer include polyesters, polypropylenes, polyethylenes, polyvinyl chlorides, polystyrenes and mixtures thereof. Preferably, the material used in the release layer is a polyester such as for example polyethylene terephthalate (PET), polypropylene terephthalate (PPT), polybutylene terephthalate (PBT), polycyclohexylene dimethylene terephthalate (PCT), or polynaphthalene terephthalate (PEN), polyethylene terephthalate (PET) being preferred. The at least one release layer may further comprise various additives such as for examples slip additives, anti-bloc additives, pigments or colorants, inorganic fillers such as calcium carbonate or talcum and foaming agents. With the aim of rendering the release layer visible, it may comprise pigments or colorants.

[0091] The thickness of the release layer will depend on the thickness of the thermoplastic layer. The release layer must be thick enough so that it is capable of being peeled off from the thermoplastic layer and so that it is not mechanically damaged during the flowing process. Typically, the release layer has a thickness in the range of about 1 to about 70 micrometers and preferably in the range of about 5 to about 50 micrometers.

[0092] In the process according to WO 2010/036406, the stack undergoes heat and pressure (thermopressing), typically by using a heating press which comprises different layers of heaters in order to maintain a constant temperature during resin flow. The stack is an assembly made of at least one fabric layer and at least one multilayer structure positioned to each other in an alternate sequence with the thermoplastic layer of the multilayer structure being in physical contact with the aramid fabric layer. The preparation of the stack can be done for example by means of two machines alternatively delivering an aramid fabric layer and one or more multilayer structures. Such machines can also comprise a system for cutting such different layers to fit the size of the heating press. The different layers of the stack are simultaneously heated in a press during a time and at a pressure and temperature sufficient to insure that the thermoplastic resin flows, saturates and encapsulates the fibers of the aramid fabric layers without substantially altering the chemical and physical properties of the release layer. Typically, the stack is pressed at a pressure between 2 and 100 bars and more preferably between 10 and 40 bars. The temperature is typically at least about 30° C. beyond the melting point of the thermo-

plastic layer to enable proper phase transitioning of the thermoplastic resin. The thermopressing time is preferably between 20 and 60 minutes and depends on the number of different layers of the stack. The impregnated composite structure is cooled, typically to 50° C., while keeping constant the pressure and then is cooled to room temperature under ambient conditions. The final product is eventually retrieved from the stack by peeling off the release layers from the impregnated composite structure.

[0093] Preferably, the thermopressing process stage of the present inventions is carried out in a plurality of steps. The number of thermopressing steps may be two, three, four or even more. In preferred embodiments, the length of each thermopressing step is from 5 to 300 or from 10 to 300 seconds with a length of about 20 seconds being particularly useful. The duration period for each thermopressing step may be the same or different. Preferably, the thermopressing pressure is from 10 to 30 bar, more preferably from 12 to 20 bar with a pressure of about 15 bar being most preferred. The pressure at each thermopressing step may be the same or different. At least two of the thermopressing steps should be carried out at a different temperature. The temperature of the first thermopressing step should be higher than the temperature of the last thermopressing step. Preferably the temperature of the first thermopressing step is in the range of from 110 to 180 C or from 130 to 180 degrees C. and that of the last thermopressing step of from 20 to 60 or from 40 to 60 degrees C. In a process involving three thermopressing steps, the second step may be carried out in the temperature range of from 110 to 180 degrees C. In a process where there are more than two thermopressing steps, the first and second steps may be carried out at the same temperature. In a process involving four thermopressing steps, the third step may be carried out in the temperature range of from 60 to 110 degrees C. In some embodiments the second thermopressing temperature is between 80 to 120 percent of that of the first thermopressing temperature. In some embodiments the third thermopressing temperature is between 40 to 70% percent of that of the first thermopressing temperature. Between each thermopressing step, the pressure on the stack is released for a period of time, for example for between 5 and 300 seconds. A period of about 20 seconds has been found to be useful. Where there are a plurality of pressure release steps, the duration of the pressure release may be the same or different.

[0094] The processing parameters should be such that the resin impregnates the fabric to an extent that between 80 to 95% of the void volume of the fabric is filled with resin.

[0095] Surprisingly, it has been found that a process comprising a plurality of short thermopressing steps can result in a much shorter overall total thermopressing time than that possible by the single processing step as described in WO 2010/036406.

[0096] Any suitable equipment can be used to carry out the thermopressing process. Vibration and ultrasonic means can also be used as potential heat sources. Multiple presses may be used to achieve the necessary number of thermopressing steps. A processing profile for a four step process is described below and is also illustrated in FIG. 1:

[0097] (1) in a first step, the stack is thermopressed at 10 to 30 bar and at a temperature of 120° C. to 170° C. for between 10 to 60 seconds followed by a pressure release period,

[0098] (2) in a second step, stack is thermopressed at 15 bar at a temperature of 143° C. for 20 seconds followed by a pressure release period,

[0099] (3) in a third step, the stack is thermopressed at 15 bar at a temperature of 84° C. for 20 seconds followed by a pressure release period, and

[0100] (4) in a fourth step, the stack is thermopressed at 15 bar at a temperature of 43° C. for 20 seconds followed by a pressure release period.

[0101] Although this is a preferred embodiment, the number of steps may be reduced or increased as well as the values of pressure, time and temperature.

[0102] As the number of thermopressing steps is reduced, the duration of these steps may need to be longer and the temperature higher. Conversely, if the number of thermopressing steps is increased, then the duration of each step may be shorter and the temperatures lower.

[0103] The method according to the present invention has numerous advantages and interests over that described in WO 2010/036406. Rather than processing batches of assembled layers, as in WO 2010/036406, it can be used on layers presented in a continuous form, for example from a roll. This allows an easier handling and less loss of material.

[0104] Also, it allows the use of conventional presses, for example one press with different temperature zones (to allow the realization of all desired thermopressing step in one pass) or a press with one single temperature zone but carrying out all steps one after the other (mainly with a change of temperature), or a succession of presses each carrying out one step in parallel. Pressing can occur by direct contact or can be generated indirectly or induced by non-contacting pressing effects such as fluid pressure from a liquid or gas.

#### Test Methods

[0105] Bending stiffness of the composite was tested on a L&W bending tester code 160 supplied by Lorentzen and Wettre, Kista, Sweden. The manufacturers prescribed test method was used.

[0106] Knife and spike resistance of an article comprising a plurality of composites of this invention was tested according to the HOSDB 07 Standard from the United Kingdom Home Office, Police Science and Development Branch (PSDB) HOSDB 07 Standards "PSDB Body Armor standards for UK Police, Part 3, Knife and Spike resistance" using a P1B test blade.

[0107] Flexural testing of the composite was tested as follows. A Zwick compression test machine was equipped with a 5 cm thick polyethylene plate having a 15 cm diameter hole. The plate was fixed with the help of holding plugs to the bottom section of the test machine in such a way that the hole was centered with the axes of the load which is also the axis of the machine. A hemispherical polyethylene punch having a diameter of 5 cm was fixed to the moving part of the traction machine. An assembly comprising thirty layers of resin impregnated composite was tested for pack flexibility. The sample dimensions were 40 cm×40 cm. The test consisted of measuring the force on the punch required to push the assembly 20 mm down through the hole.

[0108] Ballistic resistance values are reported as V50 which is a statistical measure that identifies the average velocity at which a bullet or a fragment penetrates the armor equipment in 50% of the shots, versus non penetration of the other 50%. The parameter measured is V50 at zero degrees where the degree angle refers to the obliquity of the projectile to the target. The reported values are average values for the number of shots fired for each example. V50 resistance to 9 mm full

metal jacket (FMJ) Remington bullets and 44 magnum SJHP Remington projectiles was tested to STANAG 2920. Edition 2.

[0109] Areal weights were determined according to ISO 3801. Thicknesses were measured as per ISO 5084.

#### EXAMPLES

[0110] The present invention is further defined in the following Examples. It should be understood that these examples are given by way of illustration only. All parts and percentages are by weight unless otherwise indicated. Examples prepared according to the process of the current invention are indicated by numerical values. Control or Comparative Examples are indicated by letters. Data and test results relating to the Comparative and Inventive Examples are shown in Table 1.

[0111] In Comparative Example A and Example 1, the fabric was a plain weave fabric comprising poly-p-phenylene terephthalamide yarns of 1100 dtex, commercially available from DuPont under the tradename Kevlar® merge 1K1533. The fabric had 8.5 ends/cm in both warp and weft directions and had an areal weight of 185 gsm.

[0112] In Comparative Example A and Example 1, the polymeric film was prepared by blown film extrusion. The film was a blue colored ionomer composition comprising (i) a copolymer of ethylene and 19 wt-% MAA (methacrylic acid), wherein 45% of the available carboxylic acid moieties were neutralized with sodium cations, the copolymer being obtained from DuPont under the tradename Surlyn®, and (ii) 1.1 wt-% of a color masterbatch based on an EVA matrix supplied by Elian, Oyonnax, France with the reference number M197328. The extruder temperatures were set for five extruder zones of the same length, according to a temperature profile of 176° C., 199° C., 221° C., 240° C. and 259° C. The die (63 cm wide) and the connecting pipes were set at 260° C. The chill roll was set at 12° C. The line speed was 30 m/min. The extruded film was a 55 micrometer thick layer of blue colored ionomer extrusion.

#### Comparative Example A

[0113] An assembly was made by manually stacking in order a silicone paper release layer, an extruded thermoplastic film layer, a fabric layer, an extruded thermoplastic film layer and a silicone paper release layer. Thirty of the assemblies were placed on top of each other to form a stack.

[0114] The stack was placed in a heating press (50 Ton press from SATIM) and thermopressed with the following cycle:

[0115] (a) heating the press at 105° C. for 21 minutes;

[0116] (b) inserting the stack;

[0117] (c) thermopressing the stack for 10 minutes at 135° C. and 10 bars;

[0118] (d) thermopressing the stack for 20 minutes at 135° C. and 20 bars;

[0119] (e) cooling the stack to 50° C. for 20 minutes under a pressure of 20 bars,

[0120] (f) retrieving each assembly from the stack, (g) cooling each assembly to room temperature and removing the silicone paper release layers from each assembly to leave a resin infused fabric composite.

[0121] The composite had an areal weight of 290 gsm and an average thickness of 265 micrometers. The volumetric

mass was 1094 kg/cu·m. Bending stiffness was 471.9 mNm in the machine direction and 458.6 mNm in the cross direction.

[0122] A test pack for stab resistance testing was prepared comprising twenty five layers of composite and one closed cell foam layer. The foam layer which was positioned at the back of the test pack was 3 mm thick and had an areal weight of 100 gsm. The pack was kept at room temperature for 24 hours before being tested according to the HOSDB 07 standard. A P18 test blade was used. The witness plate was foam. Each test comprised 10 drops of a new blade at 24 joules of attacking (incident) energy. There was no penetration of the blade into the witness plate, that is to say, the blade did not pass through the test pack article. A repeat test but at 36 joules of attacking energy resulted in an average blade penetration into the witness plate of 13.8 mm.

[0123] The above test was repeated but this time an SPB test spike was used. At 24 joules of attacking energy there was no penetration of the spike into the witness plate. The force required to achieve the flexural test was 2574 N.

[0124] For ballistic resistance testing, a test pack was prepared comprising thirty layers of composite adjacent to a closed cell foam layer. The foam layer which was positioned at the back of the test pack was 3 mm thick and had an areal weight of 100 gsm. Ballistic resistance was measured on dry samples conditioned at room temperature during 24 h. The V50 resistance to 9 mm FMJ bullets was 522 m/s. The V50 resistance to 44 Mag SJHP bullets was 481 m/s.

#### Example 1

[0125] An assembly was made by manually stacking in order a silicone paper release layer, an extruded thermoplastic film layer, a fabric layer, an extruded thermoplastic film layer and a silicone paper release layer as per Comparative Example A. Two of these assemblies were formed into a stack. The stack was placed in a heating press (50 Ton press from SATIM) and subjected to the following thermopressing cycle with the following cycle:

- (a) heating the press at 150° C.,
- (b) inserting the stack,
- (c) thermopressing the stack for 20 seconds at 150° C. and 15 bars,
- (d) releasing the pressure on the stack for 20 seconds by opening the press,
- (e) thermopressing the stack for 20 seconds at 150° C. and 15 bars,
- (f) releasing the pressure on the stack for 20 seconds by opening the press,
- (g) heating the press to 84° C.,
- (h) thermopressing the stack for 20 seconds at 84° C. and 15 bars,
- (i) releasing the pressure on the stack for 20 seconds by opening the press,
- (j) heating the press to 43° C.,
- (k) thermopressing the stack for 20 seconds at 43° C.,
- (l) opening the press, removing the stack from the press and removing the assemblies from the stack. Cooling the assemblies at room temperature for 10 minutes under no pressure, and
- (m) removing the silicone paper release layers from each assembly to give a resin infused fabric composite.

[0126] The composite had an areal weight of 290 gsm and an average thickness of 295 micrometers. The calculated volumetric mass was 983 kg/cu·M.

[0127] Bending stiffness of the composite was 152.1 mNm in the machine direction and 154.7 mNm in the cross-direction. This represents about a three times improvement in flexibility versus the comparative example, for the same areal density and the same composition.

[0128] Blade and spike tests similar to those for Comparative Example A were carried out. The blade test showed no penetration of the witness plate for 24 joules of attacking energy and an average blade penetration of 11.3 mm into the witness plate for 36 joules of attacking energy. These results are comparable with those of Comparative Example A.

[0129] The spike test using a SPB test spike gave no penetration at 24 joules of attacking energy again showing equivalence with the comparative example.

[0130] The force required to achieve the flexural test was 1209 N.

Ballistic tests gave a V50 resistance to 9 mm FMJ bullets of 507 m/s and a V50 resistance to 44 Mag SJHP bullets of 479 m/s. These results show that the ballistic performance of an article comprising composites of this invention is almost equivalent to that of Comparative Example 1 which is a representative example of the technology disclosed in WO2011/156577. However, the superior flexibility at the same areal weight of the inventive example when compared to the comparative example is very attractive to users. The results are summarized in Table 1.

TABLE 1

Test	Units	Comp Ex 1	Example 1
Composite Weight	gsm	290	290
Resin content (calculated)	%	36	36
process		control	New
Volumic mass (calculated)	kg/m <sup>3</sup>	1094	983
Thickness	microns	265	295
Bending Stiffness (Machine Direction)	mNm	471.9	152.1
Bending Stiffness (Cross Direction)	mNm	458.6	154.7
Average Blade Penetration P1B 36 J	mm	13.8	11.3
Average Spike Penetration SPB 24 J	mm	0	0
V50 for 9 mm projectile	m/s	522	507
V50 for 44 Mag bullet	m/s	481	479
Flexural test required force	N	9998	6306

[0131] The results demonstrate that subjecting a stack comprising only a few layers of composite components to a series of very short thermopressing cycles gives a resulting composite of greater flexibility and permits a shorter total thermopressing time when compared to a stack comprising a significantly larger number of composite components that is subjected to a single but longer thermopressing step. The personal protection properties of an article comprising a plurality of composites made by the inventive process were deemed to be acceptable.

What is claimed is:

1. A composite comprising at least one fabric and a thermoplastic polymeric resin wherein the resin is impregnated into the fabric forming a non-continuous continuum to an extent that between 80 to 95% of the maximum volumic mass (void volume) of the fabric is filled with resin.
2. A ballistic, knife or pick resistant article comprising a plurality of the composites of claim 1.
3. A method of producing a composite comprising the steps of:

- (i) providing an assembly comprising in order, a release layer, a thermoplastic resin layer, a fabric and, optionally, a second release layer,
- (ii) combining a plurality of assemblies of step (a) into a stack,
- (iii) Subjecting the stack from step (b) to a thermopressing process wherein the process comprises a minimum of two cycles where each cycle comprises
- (iv) thermopressing the stack for a defined period under a defined temperature and pressure, and
- (v) releasing the pressure on the stack for a defined period of time,
- (vi) cooling the stack,
- (vii) removing the individual assemblies from the stack, and
- (viii) removing the release layer(s) from each assembly to leave a composite, wherein the defined time periods, temperatures and pressures of each thermopressing cycle are such that the composite has between 80 to 95% of the maximum volumic mass (void volume) of the fabric filled with resin.

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**Espacenet****Bibliographic data: RS20110245 (A) — 2011-10-31**

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**BALLISTIC PROTECTIVE PLATE CAPABLE OF STOPPING 4100 J PROJECTILE AND PRODUCTION THEREOF****Inventor(s):** DRAGIC MILE [RS] ± (DRAGIĆ, Mile)**Applicant(s):** DRAGIĆ MILE [RS] ± (DRAGIĆ, Mile)**Classification:**  
- international: **B29C35/00; B32B5/02; F41H5/04**  
- cooperative:**Application number:** RS2011P000245 20050530**Priority number(s):** RS2011P000245 20050530**Also published as:** RS53652 (B1)**Abstract of RS20110245 (A)**

The invention herewith described refers to the ballistic protective plates and their production process and belongs to the field of protection devices for the vital parts of the body (chest and back part) protection against the grain bullets fired from the small arms - submachine guns, fully automatic firearms, and semi-automatic firearms, sniper rifles and carbines up to the 7,9 mm calibre and the protective plates are made of multi-layered composite material whereat the layer (1) protects the plate from mechanical damage, while the layer made of polyethylene and/or aramid fibres and/or ceramics absorbs energy of the projectile i.e. provides the ballistic protection, and the anti-trauma layer (3) reduces the deflection of the plate where the subject protective panels are made by assembling the pre-formed layers, in which process the assembled layers are mechanically processed in a press with and without heat. Ballistic protective plates are according to the invention, designed for classes III, III + and the class IV of the ballistic level protection prescribed by the standard NIJ 0101.04 U.S. National Institute of Justice, they can be produced as flat plates (for back protection), radius plates (curved at the specific radii of the curve) and as well as multiaxial plates adapted to the shape of the body.



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(54) BALLISTIC NAPE PROTECTOR FOR  
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ABSTRACT

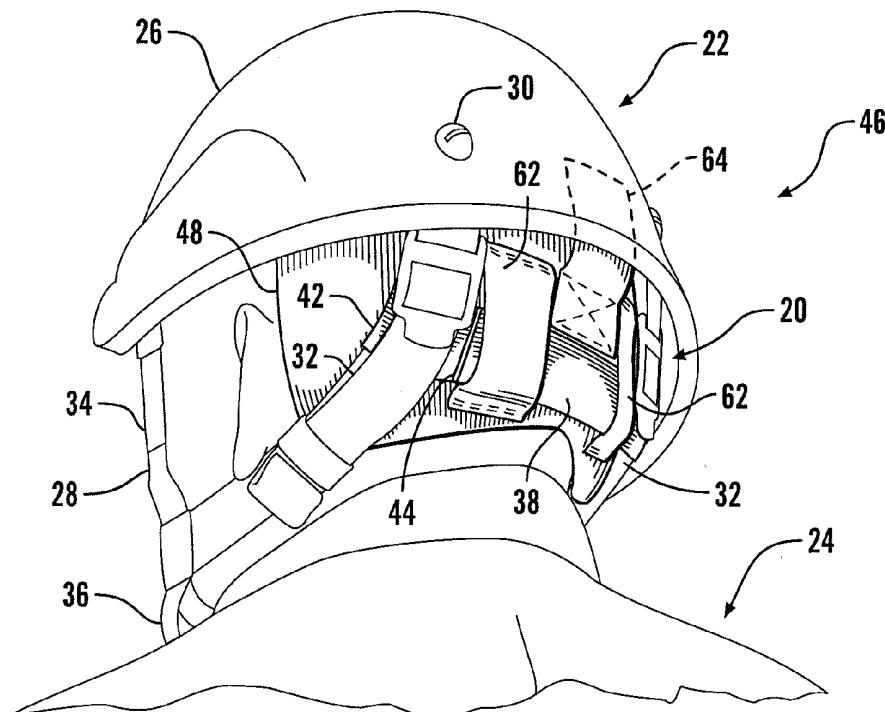
A ballistic armored component attaches to the existing retention straps of common combat helmets and provides protection to the otherwise exposed lower skull and upper neck region. A fabric covering contains a soft armor or hard armor insert, and is mounted by straps or other fasteners to existing straps found in conventional helmets. The armor component may be fabric of aramid fibers, or fabric of ultra high molecular weight polyethylene fibers, or may be fabricated of a rigid plate of ceramic, polymer, or metal. The armored component adds additional protection from ground-level or subterranean munitions, by placing a ballistic shape on the lower skull region (occipital region), providing significant additional ballistic coverage with minimal weight and bulk. The fabric shell may also be connected directly to the helmet shell, to allow the component to withdraw within the helmet when the wearer's neck is flexed rearwardly.

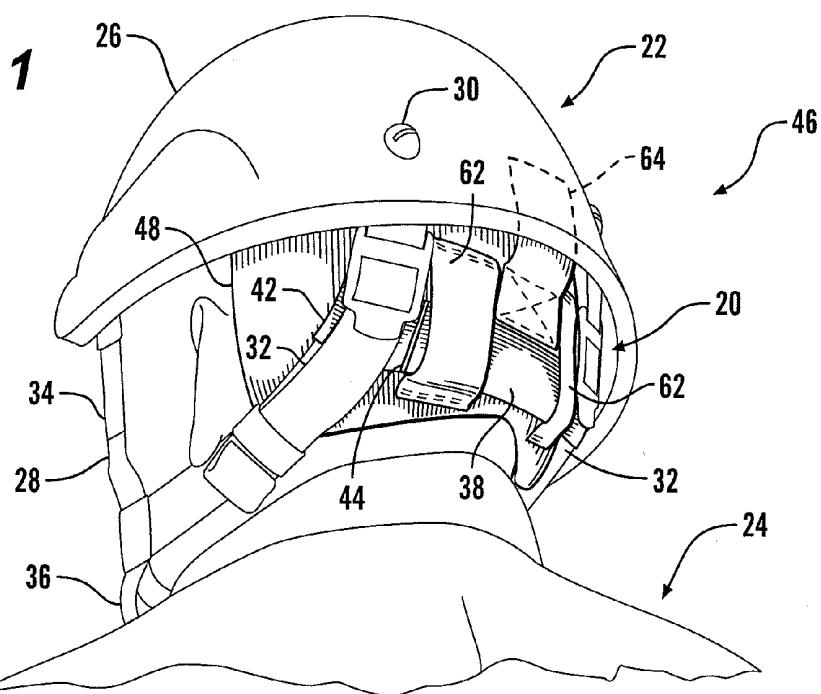
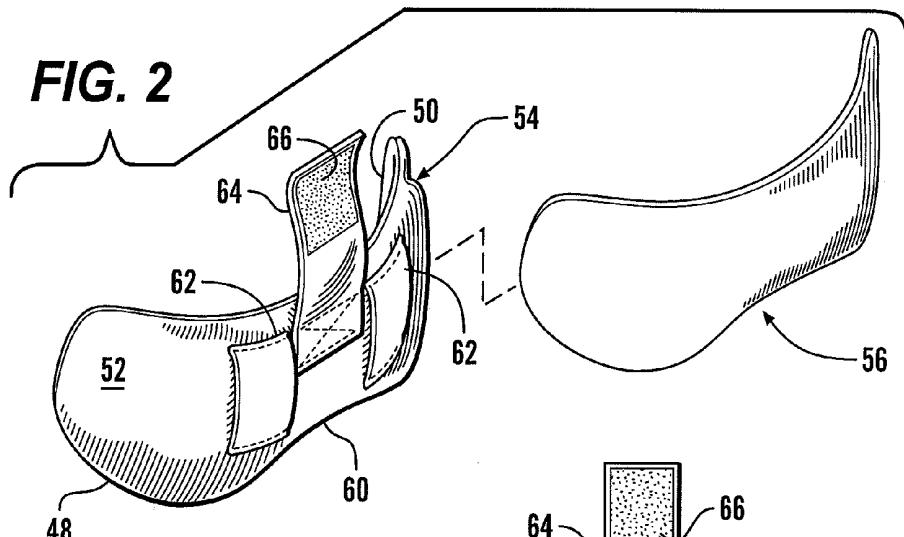
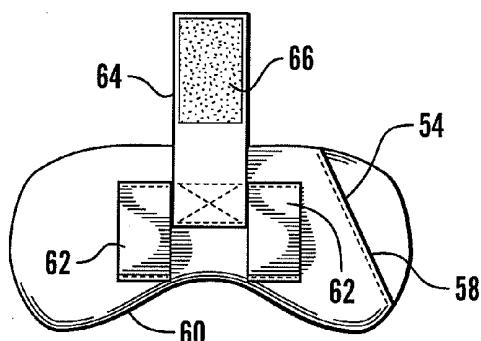
(21) Appl. No.: 14/970,005

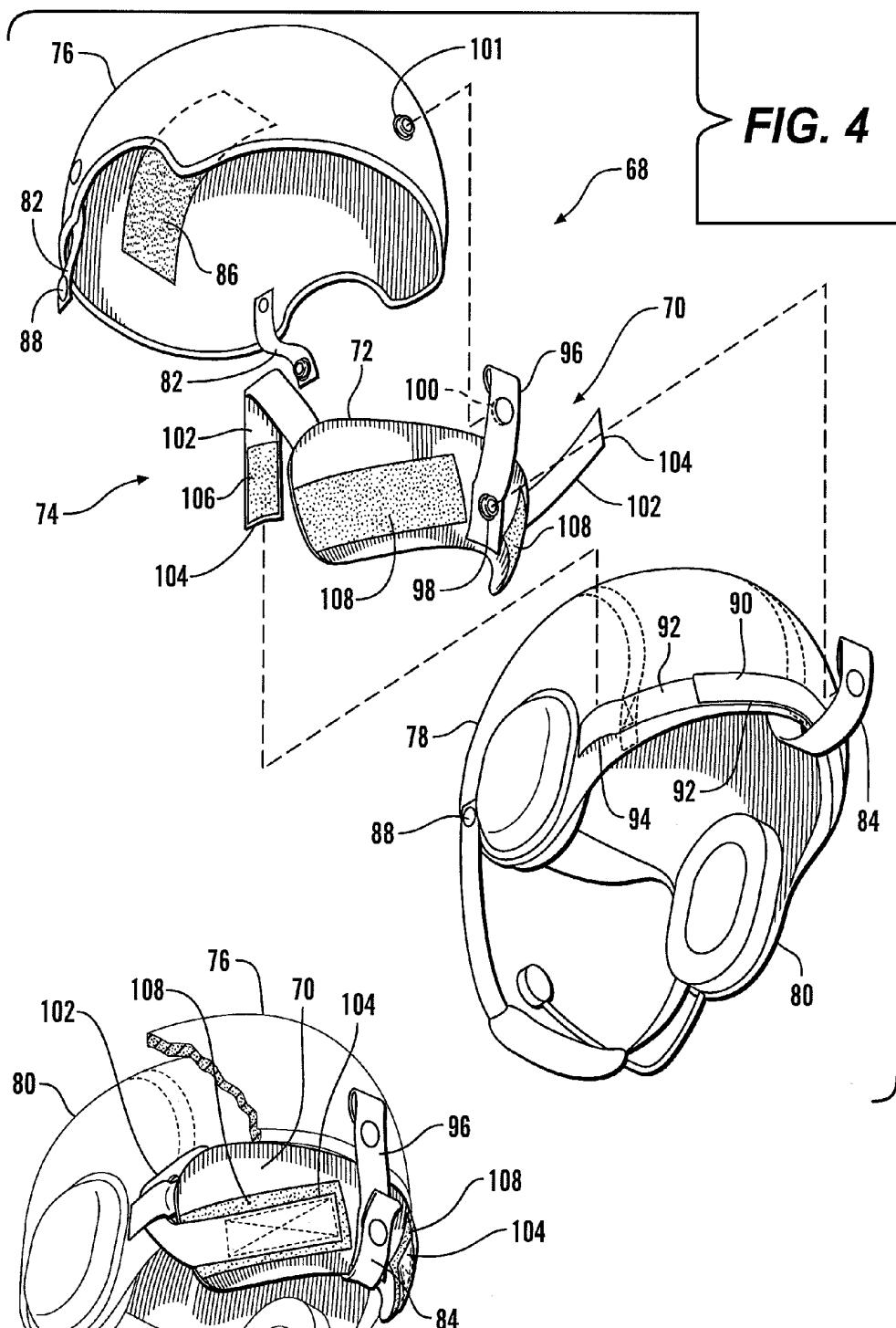
(22) Filed: Dec. 15, 2015

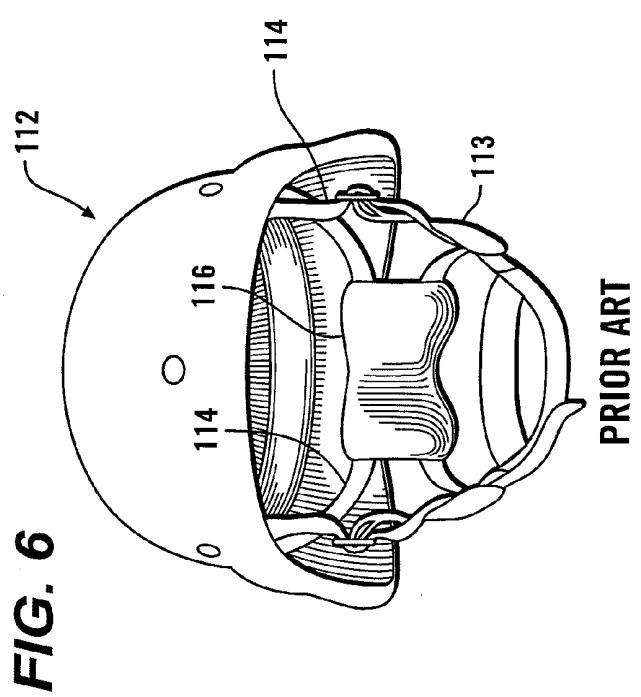
Related U.S. Application Data

- (63) Continuation of application No. 13/936,613, filed on Jul. 8, 2013, now Pat. No. 9,243,872, which is a continuation of application No. 11/681,399, filed on Mar. 2, 2007, now Pat. No. 8,505,113.  
(60) Provisional application No. 60/778,552, filed on Mar. 2, 2006.

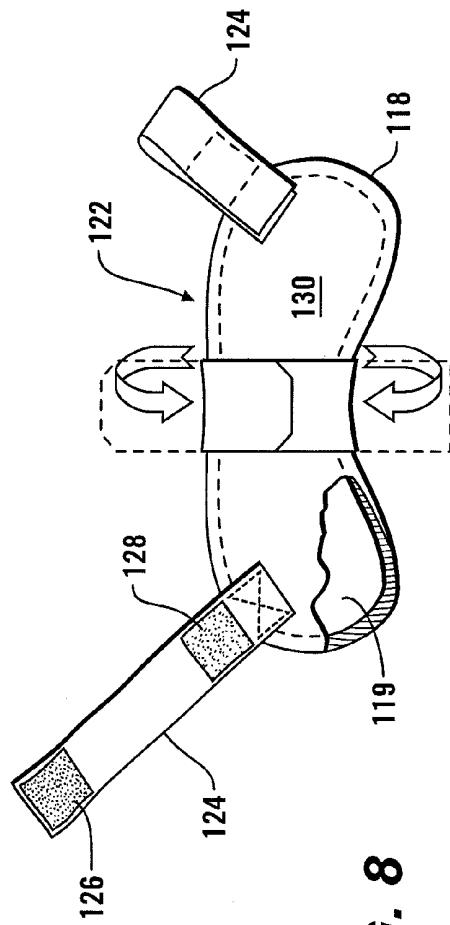
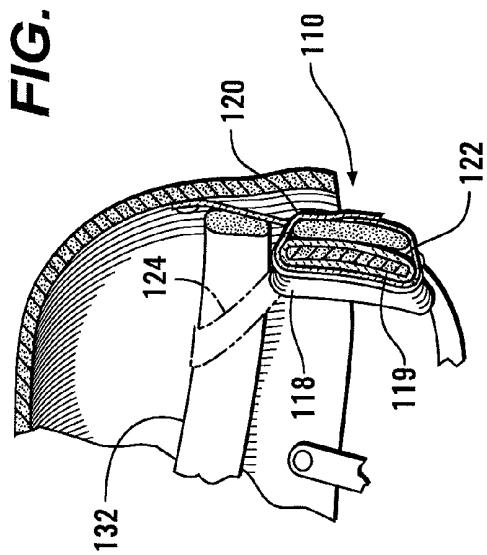


**FIG. 1****FIG. 2****FIG. 3**

**FIG. 5**



**FIG. 7**



**FIG. 8**

## BALLISTIC NAPE PROTECTOR FOR BALLISTIC HELMET

### CROSS REFERENCES TO RELATED APPLICATIONS

[0001] This application is a continuation of U.S. application Ser. No. 13/936,613, filed Jul. 8, 2013, which is a continuation of U.S. application Ser. No. 11/681,399, filed Mar. 2, 2007, now U.S. Pat. No. 8,505,113, which claims benefit from U.S. provisional app. 60/778,552, filed Mar. 2, 2006, the disclosures of which applications are hereby incorporated by reference herein.

### STATEMENT AS TO RIGHTS TO INVENTIONS MADE UNDER FEDERALLY SPONSORED RESEARCH AND DEVELOPMENT

[0002] Not applicable.

### BACKGROUND OF THE INVENTION

[0003] The present invention relates to body armor systems worn for protection against projectile threats such as rifle and handgun bullets, and shrapnel.

[0004] Persons exposed to projectile threats, such as police officers and soldiers, may seek a certain level of protection by wearing armored clothing. Low velocity projectiles such as handgun rounds, fragmentation rounds from a grenade or mortar, and miscellaneous shrapnel may be countered by so-called "soft armor." Soft armor is worn in the form of jackets, vests, etc. which are composed of assemblies of ballistic fabric such as those formed from DuPont Kevlar® fibers or of Spectra® ultra high molecular weight polyethylene fibers from Honeywell. The soft armor is often fabricated as flexible panels which are received within pockets or pouches formed in fabric vests or jackets. In more serious threat situations, where higher velocity rifle rounds and fragments must be countered, soft armor has typically been supplemented with hard armor fabricated of rigid plates of ceramic, polymer, or metal.

[0005] Most Ballistic helmets in use today are flared at the lower edge. This shape makes the helmets easier to produce by allowing single direction molds and also aids in airflow under the helmet, and may in some circumstances allow greater range of motion. Although this flared shape may be helpful in defending against air-bursting munitions traveling downward toward the wearer from a point above, this shape leaves the serviceman's head exposed to projectiles coming from ground-level or subterranean munitions—a significant threat in certain modern conflict situations. A projectile from such a munition typically travels towards the wearer with an upward angle of incidence. A helmet with a flared lower edge exposes significant portions of the head and upper neck to this upwardly traveling threat.

[0006] What is needed is a ballistic helmet assembly which protects the lower skull and upper neck region of a wearer while preserving necessary range of motion, and which can be retrofitted to existing helmet systems.

### SUMMARY OF THE INVENTION

[0007] The ballistic helmet assembly of this invention has a ballistic armored component that attaches to the existing retention straps of common combat helmets and provides protection to the otherwise exposed lower skull and upper neck region. The component may comprise a fabric coverings

which contains a soft armor or hard armor insert. The component has straps or other fasteners which allow for removable attachment to existing straps found in conventional helmets. The invention adds additional protection from ground-level or subterranean munitions, by placing a ballistic shape on the lower skull region (occipital region). In doing so, a significant amount of ballistic coverage can be achieved with minimal weight and bulk. Moreover, replacement or new retention assemblies can be provided with the nape protecting component integrated therewith.

[0008] In some current combat situations, the primary threats being encountered are high speed fragments from ground-based explosions. While certain fragments cannot be stopped, even by thick steel plate, many fragments that would otherwise kill or severely injure a human can be stopped by an attached ballistic component, for example small fragments traveling at high speeds. Protecting the base of the skull protects large portions of the brain stem, cerebellum, occipital lobe, and temporal lobe. These regions control highly important functions. Breathing, sight, locomotion, and language are all functions that reside in this area.

[0009] It is an object of the present invention to provide a lightweight protective element which can assist in protecting soldiers from ground based or subterranean munitions.

[0010] It is an additional object of the present invention to provide a protective element for the base of the skull which can be rapidly attached to and removed from an existing helmet.

[0011] Further objects, features and advantages of the invention will be apparent from the following detailed description when taken in conjunction with the accompanying drawings.

### BRIEF DESCRIPTION OF THE DRAWINGS

[0012] FIG. 1 is a rear perspective view, looking upwardly at the ballistic assembly of this invention installed in a U.S. Army Advanced Combat Helmet.

[0013] FIG. 2 is an exploded rear perspective view, looking downwardly at the nape protecting component of the assembly of FIG. 1, with the ballistic element shown exploded from its fabric covering.

[0014] FIG. 3 is a rear elevational view of the nape protecting component of FIG. 2.

[0015] FIG. 4 is an exploded rear perspective view of a combat vehicle crewman helmet, showing the position of an alternative embodiment nape protective component of this invention.

[0016] FIG. 5 is a rear perspective view of the assembly of FIG. 4, with the helmet shell partially broken away in section, shown the attachment of the nape protective component to the cap.

[0017] FIG. 6 is a front perspective view of a U.S. Marine Corps helmet.

[0018] FIG. 7 is a fragmentary side cross-sectional view of the helmet of FIG. 6 with an alternative embodiment nape protecting component attached to the nape pad of the helmet retention assembly.

[0019] FIG. 8 is a rear elevational view of an alternative embodiment nape protecting component, adding side straps to the nape protecting component of FIG. 7, partially broken away in section to show the ballistic element therein.

### DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0020] Referring more particularly to FIGS. 1-8, wherein like numbers refer to similar parts, a nape protecting component 20 of this invention is mounted to a ballistic combat helmet 22 and is worn by a soldier 24. The nape protecting component 20 shown in FIGS. 1-3 is configured for use with a conventional US Army Advanced Combat Helmet (ACH) such as those manufactured by Mine Safety Appliances Company, of Pittsburgh, and shown in U.S. Pat. D449,411, the disclosure of which is incorporated by reference herein.

[0021] The ACH helmet has a stiff ballistic shell 26 provided with a pad suspension system, not shown, and a chinstrap retention system 28 with hardware 30 which fastens the retention system to the shell. The chinstrap retention system 28 has two downwardly extending rear retention straps 32 or rear legs which are connected to the helmet ballistic shell 26 by the hardware 30, and which are provided with various buckles which permit the overall length of the retention straps to be adjusted. The rear retention straps 32 extend forwardly to be connected to two front retention straps 34 and a chin strap 36. The two rear retention straps 32 are connected by a nape strap 38, as shown in FIG. 1. The nape strap 38 is a sidewardly extending strap with a loop 42 on one end through which one of the rear retention straps 32 extend, the other end 44 of the nape strap extends behind the other rear retention strap, and is then folded back on itself and secured in place by a two-part hook and loop fastener such as VELCRO® fastener manufactured by Velcro Industries B.V.

[0022] The conventional pad suspension system is comprised of a number of resilient pads which have one part of hook and loop fastener on the surface which faces the interior of the helmet shell. The interior of the shell is provided with an array of patches of the other part of the hook and loop fastener, such that the pads may be inserted and attached at the desired locations.

[0023] The nape protecting component 20 is readily connected to the conventional helmet assembly to form a ballistic helmet assembly 46 with added protection to the lower skull and nape of the neck. As best shown in FIG. 2, the nape protecting component 20 has a fabric covering 48 in an oblong shape, the covering has a front sheet 50 which is sewn to a rear sheet 52 to define a pocket 54 which receives a ballistic element 56 therein. By "ballistic element" is meant an element of soft or hard armor, configured to resist ballistic projectiles or fragments. The ballistic element 56 may be conventional soft armor, i.e., assemblies of ballistic fabric such as those formed from DuPont Kevlar® fibers, fibers of Spectra ultra high molecular weight polyethylene fibers from Honeywell, or other ballistic material, or hard armor, for example elements fabricated of rigid plates of ceramic, polymer, or metal. Moreover, because the ballistic inserts are replaceable elements, the nape protecting component 20 may be readily updated with more advanced materials as they become available. A rifle-level protection is envisioned with enhanced materials, for example with ceramic or metal. The fabric covering 48 may be sewn with an upwardly extending slot 58, as shown in FIG. 3, to permit the insertion and removal of the ballistic element 56. The front sheet 50 of the fabric covering may be a different material than the rear sheet 52, for example the front sheet may be a brushed perforated fabric such as spacer mesh to promote wicking and avoid abrasion to the back of the wearer's neck, while the rear sheet may be a more durable material such as nylon, cotton/nylon,

or DuPont's NOMEX® resistant meta-aramid material, or other fabric, and may have a camouflage design placed thereon.

[0024] The fabric covering with interior ballistic element 56 is longer than it is tall, for example about eight inches wide, and from two-and-a-half to three inches tall, however, it may be produced in a number of sizes to suit the range of servicemen who will use the device. Preferably, in order to preserve hearing, the component 20 will extend from behind one ear to just behind the other ear in the side to side direction, and will extend vertically from a position about one inch above the lower rim of the helmet shell to a position about one inch above the wearer's collar. The lower edge 60 of the fabric covering 48 may have a downwardly opening concave contour, to better conform to the wearer's neck. The entire component 20 may be somewhat flexible, depending on the composition of the ballistic element 56, but is generally concave towards the wearer, so that the sides of the component wrap around the head of the wearer.

[0025] As shown in FIGS. 2 and 3, two short upwardly extending strips of webbing are sewn to the rear sheet 52 of the fabric covering 48 to define two sidewardly spaced loops 62 which are large enough to permit free end 44 of the nape strap 38 to be threaded therethrough. The loops 62 may be spaced about one-and-a-half inches apart. Between the two loops 62, a helmet mounting strap 64 is sewn to the rear sheet 52 of the fabric covering 48. The helmet mounting strap 64, as shown in FIG. 1, extends upwardly and has one part of a two-part hook and loop fastener, for example the loop part, on a rearwardly facing surface 66 for attachment to the interior of the helmet shell 26. The helmet mounting strap 64 may be, for example, about four inches long, extending about three inches upward from the fabric covering 48.

[0026] The nape protecting component 20 readily attaches to the existing helmet straps and is very unobtrusive to the wearer, while providing significant additional ballistic protection. To mount the component 20, the free end 44 of the conventional nape strap 38 is released from its hook-and-loop fastener attachment to itself. Typically, a conventional pad will be mounted on the nape strap 38, if so this pad may be removed and will not be needed when the nape protecting component 20 is in use. In addition, one of the helmet suspension pads, not shown, is temporarily removed from the rear interior surface of the helmet shell 26. The nape strap 38, which is connected at one end to a first rear retention strap 32, is threaded through the two loops 62, around the second rear retention strap 32, and then secured to itself with the hook-and-loop closure adjacent the first rear retention strap. The helmet mounting strap 64 is extended upwardly within the helmet shell 26, and is attached by pressing together the hook-and-loop fastener to a patch, not shown, on the interior of the helmet. The removed helmet suspension pad is then reattached, but at least one inch above the termination of the helmet mounting strap 64, thereby leaving a space for the nape protecting component 20 to slide upwardly into the helmet when the wearer arches back his neck.

[0027] The illustrated nape protecting component is sized to allow the wearer to use earphone-based communications equipment. It may extend downwardly a greater distance, although with some interference with neck mobility. An enlarged nape protecting component may be employed where additional protection is required, and the loss in mobility and versatility is acceptable.

[0028] An alternative embodiment ballistic helmet assembly 68 is shown in FIGS. 4 and 5. The nape protecting component 70, like the component 20 discussed above, has a fabric covering 72 with a ballistic element contained therein, not shown. The fabric covering 72 also has an upwardly extending slot, not shown, which is positioned on the front surface of the fabric covering to permit the insertion and removal of the ballistic element. The nape protecting component 70 is configured to work with a conventional two-part helmet system 74 such as the combat vehicle crewman (CVC) helmet, such as is available from Sonetronics, West Belmar, New Jersey, which has a ballistic shell 76 to which is mounted a flexible liner or cap 78 having an integral headset 80 with attached microphone. The cap 78 is connected to the shell 76 by two front retention straps 82, which are fixed at one end to the shell; a single rear retention strap 84 which is fixed at one end to the cap; and a two-part hook and loop fastener having a patch on the top of the cap, not shown, and a patch 86 on the underside of the helmet shell 76. Each retention strap 82, 84 has one element of a two-part snap fastener 88 on its free end.

[0029] The cap 78 has a rear nape strap 90 which is comprised of two separate nape strap segments 92 which are sewn to the cap at one end, and which have overlapping hook and loop fastener to permit the length of the nape strap 90 to be adjusted. Adjacent the fixed ends of the nape strap segments 92 are loops 94 of the nape strap segments which open upwardly and downwardly, near each headset 80 speaker 95.

[0030] The nape protecting component 70 has an upwardly extending helmet mounting strap 96 with the male part 98 of a two-part snap fastener mounted at the base of the strap where it is fixed to the fabric covering 72 of the nape protecting component. The free end of the helmet mounting strap 96 has the female part 100 of a two-part snap fastener mounted thereto. As shown in FIG. 5, the cap rear retention strap 84 extends from the cap and is snapped into engagement with the snap 98 on the mounting strap, and is thus not connected directly to the helmet shell. The helmet mounting strap 96 free end is snapped into engagement with the snap fastener 101 on the helmet shell intended for the cap rear retention strap 84.

[0031] The nape protecting component 70 has two flexible straps 102 that extend from the front of the fabric covering 72 at about a 45 degree angle from the vertical. Each strap 102 is about five and one-half inches long and extends downwardly through one of the nape strap segment 92 loops 94 on the cap 78. Each strap 102 passes through a loop 94, and is then reversed to extend upwardly and overlie the rear surface of the fabric covering. Each strap 102 free end 104 has a patch 106 of one part of a hook and loop fastener, and is secured in place by engaging with a patch 108 of the other part of the hook and loop fastener which is fixed to the rear surface of the fabric covering, extending upwardly at about a 45 degree angle, and about three and one-half inches long. The nape protecting component 70 is thus readily attached to the helmet system 74 in such a way that it can be displaced upwardly on the interior of the helmet shell, but yet is still prevented from descending too low, or moving undesirably to the side.

[0032] Another alternative embodiment nape protecting component 110 is shown in FIG. 7 for use with a prior art helmet such as the USMC LW helmet 112, shown in FIG. 6. Such a helmet 112 is manufactured by Gentex Corporation of Simpson, Pa., for the United States Marine Corps, and has a four-point retention harness 113 with two downwardly extending retention straps 114 with a standard nape pad 116 attached thereto. The nape pad 116 also constitutes a strap,

although in this case it has a cushioning padding. A variation 122 of the component for the helmet 112, which is identical to the component 110 but a larger size with side straps 124, is shown in FIG. 8. The nape protecting component 110, as shown in FIG. 7 has a fabric covering 118 similar in shape to the nape protecting components discussed above, with a similar ballistic element 119 retained therein. The nape protecting component 110 is secured to the retention harness 113 by two attachment straps 120, 121 which are sewn to the fabric covering 118 in the center of the component 110. The first attachment strap 120 is attached along an upper seam, and the second attachment strap 121 is attached along a lower seam, and each of the attachment straps has one half of a hook and loop fastener, such that when the fabric covering and ballistic element 119 are positioned frontwardly of the helmet's nape pad 116, the two attachment straps encircle the nape pad and are secured to one another to position the nape protecting component as desired.

[0033] For use with larger size USMC LW helmets, a nape protecting component 122, similar to the component 110 is used, but which is larger and provided with two side attachment straps 124, as shown in FIG. 8. Each side attachment strap 124 extends upwardly and outwardly from the fabric covering, and has a first patch 126 and a second patch 128 of mating hook and loop material. Alternatively, the second patch may be sewn to the rearwardly facing surface 130 of the fabric covering 118. As shown in phantom view in FIG. 7, the side attachment straps 124 extend upwardly and loop around existing straps or bands 132 which extend rearwardly from the front retention harness attachment points to the rear attachment points. The side attachment straps 124 are then looped back on themselves to form closed loops.

[0034] It should be noted that various alternative closures and fastening assemblies may be used in place of the hook and loop fasteners shown, for example where appropriate snaps, ties, buttons, quick-release plastic buckles or clips, metal or plastic buckles, and lacing.

[0035] It should be noted that the ballistic element may be formed as a stack of multiple layers of ballistic material, for example material of Kevlar® fibers. Or, for example, layers of Spectra® fiber material may be stitched around the periphery to form a stiffer ballistic element. If additional stiffness is desired, a stiffening formed plastic element may be employed with the ballistic element, or may be adhered or stitched to the ballistic element as disclosed in U.S. Pat. No. 6,892,392, the disclosure of which is incorporated by reference herein. The stitching may be around the perimeter, or in a quilted or other pattern. The greater stiffness of the nape protecting component can help in stabilizing the entire helmet assembly, simply by providing a greater stable surface area against the head. This can be particularly advantageous when equipment is mounted to the front of the helmet, such as night vision goggles, etc.

[0036] It should be further noted that the ballistic element may be enclosed in a sewn lightweight fabric bag, to protect it from abrasion and soiling.

[0037] It is understood that the invention is not limited to the particular construction and arrangement of parts herein illustrated and described, but embraces all such modified forms thereof as come within the scope of the following claims.

We claim:

1. A helmet and ballistic armor assembly for protecting portions of the lower skull and upper neck region of a wearer against ballistic projectiles and shrapnel, comprising:
  - a protective helmet having an upper ballistic shell, and a helmet retention assembly having two downwardly extending rear retention straps which are connected to the shell and which extend downwardly below the shell at a rear of the helmet, the helmet retention assembly having a first member which extends between and is connected to the two rear retention straps;
  - a ballistic armor assembly comprising:
    - a ballistic armor element formed of ballistic material, the ballistic material being selected from the group consisting of fabric of aramid fibers, and fabric of ultra high molecular weight polyethylene fibers; and
    - connecting elements connected to the ballistic armor element which engage portions of the helmet retention assembly two rear retention straps or first member, the ballistic armor assembly thereby being connected to the retention assembly for movement with respect to the shell so the ballistic armor assembly may slide upwardly into the shell when the wearer's neck is arched back.
2. The ballistic armor assembly of claim 1 further comprising a first fastener fixed to a flexible first strap which extends upwardly from the ballistic armor assembly, the first fastener connected to the upper ballistic shell, and being flexible to allow the ballistic armor element to be displaced upwardly within the upper ballistic shell of the protective helmet.
3. The ballistic armor assembly of claim 2 wherein the first fastener comprises one part of a hook and loop fastener, the other part of the hook and loop fastener being secured to the interior of the upper ballistic shell.
4. The ballistic armor assembly of claim 2 further comprising two loops spaced from each other mounted rearwardly from and connected to the ballistic armor assembly, the two loops receiving therein the first member which is connected at each end to a downwardly extending one of the rear retention straps.
5. A helmet and ballistic armor assembly for protecting portions of the lower skull and upper neck region of a wearer against ballistic projectiles and shrapnel, comprising:
  - a protective helmet having an upper ballistic shell, and a helmet retention assembly having two downwardly extending rear retention straps which are connected to the shell and which extend downwardly below the shell at a rear of the helmet, the helmet retention assembly having a first member which extends between and is connected to the two rear retention straps;
  - a ballistic armor assembly comprising:
    - a covering defining a pocket therein, the covering configured to extend along the rear and opposite sides of a head of the wearer;
    - a ballistic armor element comprised of soft or hard armor configured to resist ballistic projectiles or fragments, wherein the ballistic armor element is received within the pocket; and
    - a plurality of straps connected to the covering which engage portions of the helmet retention assembly two rear retention straps or first member, the ballistic armor assembly thereby being connected to the retention assembly for movement with respect to the shell so the ballistic armor assembly may slide upwardly into the shell when the wearer's neck is arched back.
6. The ballistic armor assembly of claim 5 further comprising a slit opening in the covering through which the ballistic armor element is insertable into an interior of the covering.
7. The ballistic armor assembly of claim 5 further comprising two auxiliary loops which extend upwardly and sidewardly from the covering and which each engage portions of the helmet retention assembly.
8. The ballistic armor assembly of claim 5 further comprising a first fastener fixed to a flexible first strap which extends upwardly from the ballistic armor assembly, the first fastener connected to the upper ballistic shell, and being flexible to allow the ballistic armor element to be displaced upwardly within the upper ballistic shell of the protective helmet.
9. The ballistic armor assembly of claim 8 wherein the first fastener comprises one part of a hook and loop fastener, the other part of the hook and loop fastener being secured to the interior of the upper ballistic shell.
10. The ballistic armor assembly of claim 5 further comprising two loops spaced from each other mounted to a rear of the covering, the two loops receiving therein the first member which is connected at each end to a downwardly extending one of the rear retention straps.
11. A helmet and ballistic armor assembly for protecting portions of the lower skull and upper neck region of a wearer against ballistic projectiles and shrapnel, comprising:
  - a protective helmet having an upper ballistic shell, a flexible cap received within the upper ballistic shell and having loops attached thereto which open upwardly and downwardly;
  - a ballistic armor assembly comprising:
    - a covering defining a pocket therein, the covering configured to extend along the rear and opposite sides of a head of the wearer;
    - a ballistic armor element comprised of a stack of multiple layers of ballistic material, the ballistic material being selected from the group consisting of: fabric of aramid fibers, and fabric of ultra high molecular weight polyethylene fibers, wherein the ballistic armor element is received within the pocket; and
    - a plurality of straps connected to the covering, wherein one of said straps engages each of the cap loops, and one of said straps comprises a mounting strap which directly engages the upper ballistic shell, the ballistic armor assembly thereby being connected for movement with respect to the shell so the ballistic armor assembly may slide upwardly into the shell when the wearer's neck is arched back.
12. The assembly of claim 11 wherein the mounting strap extends upwardly from the covering, and having attached thereto one half of a two-part snap fastener, the other half of the two-part snap fastener being fixed to an exterior of the upper ballistic shell.
13. The assembly of claim 11 further comprising a slit opening in the covering through which the ballistic armor element is insertable into an interior of the covering.
14. The assembly of claim 11, wherein the covering has a front sheet comprised of a spacer mesh positioned towards a helmet front.
15. A method for providing a helmet with ballistic armor for protecting portions of the lower skull and upper neck region of a wearer against ballistic projectiles and shrapnel, the method comprising:
  - engaging a protective helmet having an upper ballistic shell, and a helmet retention assembly having two down-

wardly extending rear retention straps which are connected to the shell and which extend downwardly below the shell at a rear of the helmet, the helmet retention assembly having a first member which extends between and is connected to the two rear retention straps, the retention assembly having connected thereto a nape pad at the rear of the helmet;

attaching a ballistic armor assembly comprising a ballistic armor element formed of ballistic material comprising soft armor or hard armor to the helmet retention assembly two rear retention straps or first member in a manner which permits movement of the ballistic armor element with respect to the upper ballistic shell so the ballistic armor assembly may slide upwardly into the shell when a wearer's neck is arched back.

**16.** The method of claim **15** wherein the ballistic material is selected from the group consisting of fabric of aramid fibers, and fabric of ultra high molecular weight polyethylene fibers.

**17.** The method of claim **15** wherein the step of attaching the ballistic armor assembly is preceded by removing the nape pad from its position connected to the retention assembly and replacing the removed nape pad with the ballistic armor assembly.

**18.** The method of claim **15** wherein the step of attaching the ballistic armor assembly comprises positioning the ballistic armor assembly frontwardly of the nape pad and securing it with respect thereto.

\* \* \* \* \*



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(54) **COMPOSITE PANEL FOR ARMOR  
SHIELDING OF VEHICLES**

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**F41H 7/02** (2006.01)

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CPC ..... **F41H 5/0421** (2013.01); **F41H 7/02**  
(2013.01); **F41H 5/0428** (2013.01)

USPC ..... **89/36.02**

(57) **ABSTRACT**

Armor panel comprising an aluminium alloy plate wherein:  
a) said aluminium alloy has the following chemical composition expressed in percentages per weight:

$5.1\% \leq Zn \leq 9.7\%$

$1.5\% \leq Mg \leq 2.9\%$

$1.2\% \leq Cu \leq 2.1\%$

$Si \leq 0.4\%$

$Fe \leq 0.5\%$

$Mn \leq 0.3\%$

$Cr \leq 0.28\%$

$Ti \leq 0.2\%$

$Zr \leq 0.15\%$

b) said plate comprises a face oriented towards the shocks and a face opposite said face oriented towards the shocks coated with a composite reinforcing layer comprising reinforcing fibres or bands with high ballistic protection performance, typically made of high mechanical performance glass, aramid or high performance polyethylene.

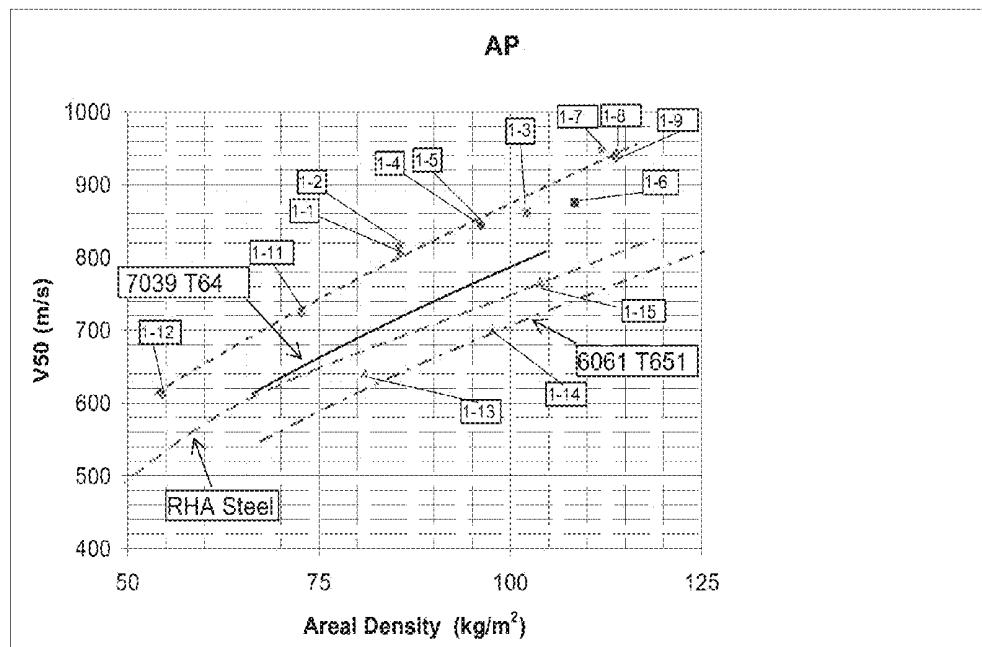


Figure 1

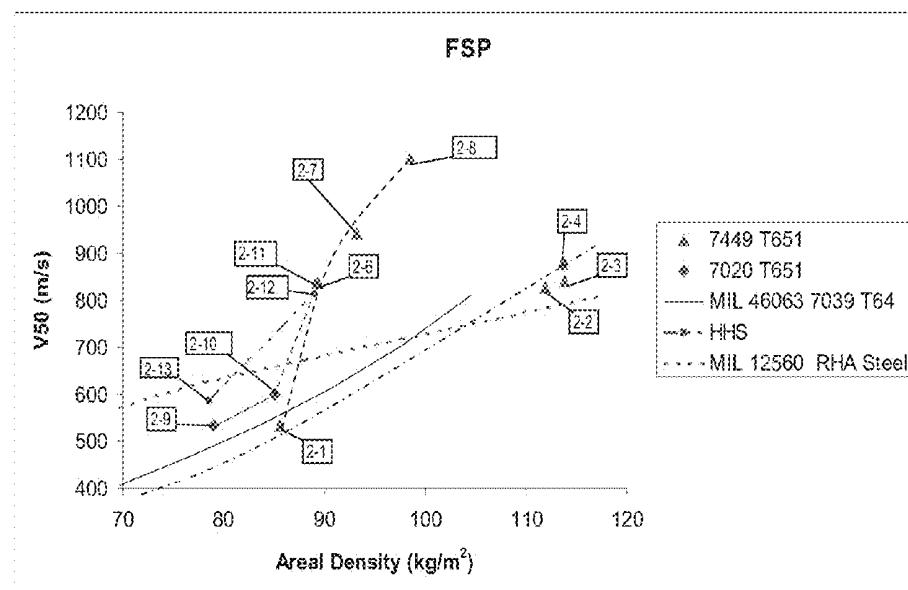


Figure 2

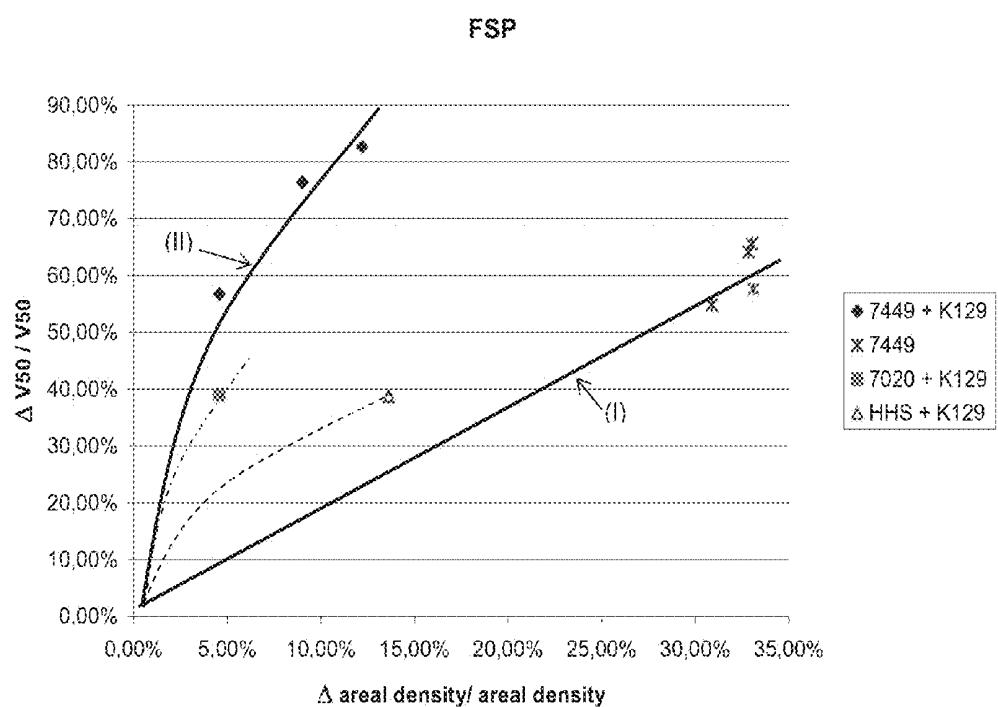


Figure 3

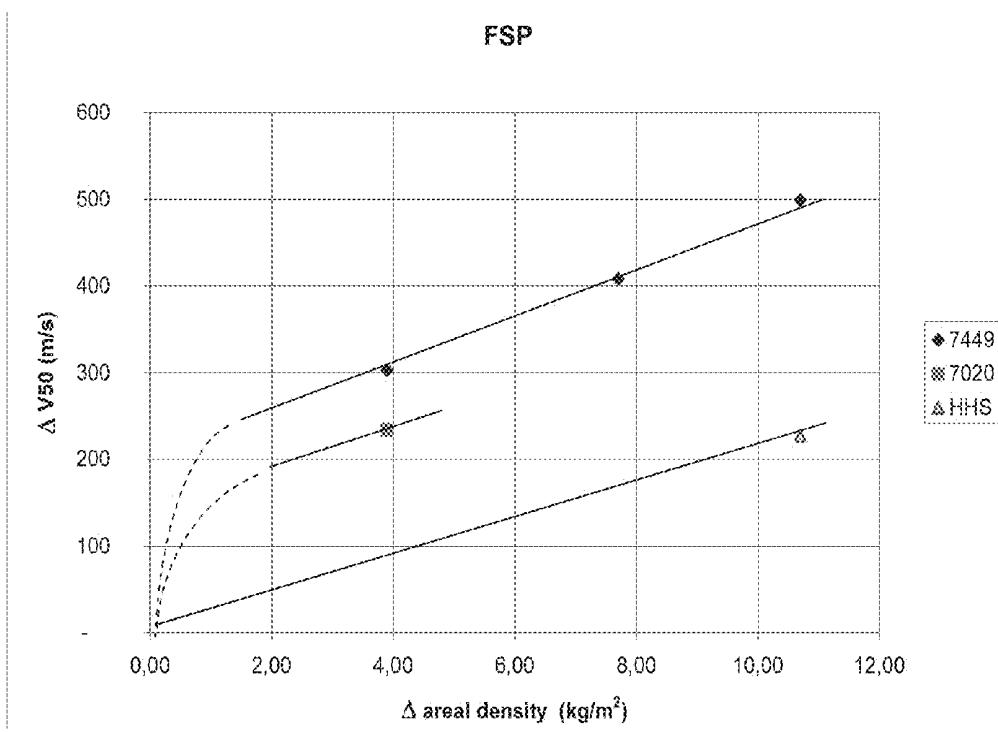


Figure 4

## COMPOSITE PANEL FOR ARMOR SHIELDING OF VEHICLES

### CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to FR 13002111.6 filed Apr. 22, 2013 the content of which is incorporated herein by reference in its entirety.

### BACKGROUND

[0002] 1. Field of the Invention

[0003] The invention relates to the manufacture of armor shielding panels for the protection of vehicles from perforating projectiles and fragments projected during an impact.

[0004] 2. Description of Related Art

[0005] In general, an armor shield comprises a metal panel typically made of steel, aluminium, titanium or alloys of these metals. Such panels usually have an excellent capacity for absorption of the kinetic energy of the perforating projectile during an impact. However, in particular if they are made of steel or a titanium alloy, such panels are heavy and consequently have a low efficiency in terms of energy absorption relative to the weight transported by a vehicle. Titanium alloy panels usually give the best armor shielding protection but they are very expensive and heavy.

[0006] The armor shielding panel has a face exposed to impacts and a rear face. When there is an impact on a metallic armor panel, the armor-piercing projectile might be stopped completely in the panel but damage to the rear face of the panel can cause the formation of fragments which can become more dangerous than the projectile stopped by the panel when they are violently ejected from the panel (towards the inside of the vehicle).

[0007] Composite panels have been developed that have a greater projectile stopping capacity and lower sensitivity to fragmentation, thus giving better performances relative to the weight transported by the vehicle. But these are composite products comprising ceramic products placed on the face exposed to shocks of a support plate, itself composite, usually based on carbon, glass and polymers with a high molecular weight. Such products are very expensive.

[0008] The efficiency of armor panels is usually characterised by two types of tests. The first test is designed to quantify their capacity to stop piercing projectiles. This is referred to as "AP" ("Armour Piercing") and characterises the resistance to perforation. The second test is designed to quantify their capability to withstand the impacts of fragmented debris. This second type of test is referred to as "FSP" ("Fragment Simulated Projectiles"). During these tests, the armor panels are the target of different shaped projectiles (spindle shape for the AP test, larger and more squat form projectiles for FSP tests). In each type of test, several projectile geometries are used depending on the thickness of the tested panel and the nature of the threats that said armor panel is designed to protect.

[0009] For both tests, the capacity to stop projectiles and absorb their kinetic energy without emitting dangerous debris is quantified by a velocity V50 that is defined for example in standard MIL-STD-66; V50 is the average velocity reached by projectiles at the time of the impact obtained using an equal number of results with the highest partial penetration velocities and results with the lowest complete penetration velocities, the velocity being imposed within a specified range.

[0010] In general, the material from which the armor panel is made rarely has a good AP-FSP compromise, regardless of whether it is a ceramic, steel, an aluminium alloy or titanium alloy. When it has good resistance to armor piercing, its FSP resistance is often mediocre. Conversely, a material with good FSP resistance often has mediocre AP resistance.

[0011] Patent application US2011/0252956 discloses metallic armor panels composed of at least two layers of different aluminium alloys that are metallurgically bonded together. The intimate metallurgical bond between these two layers typically results from transformation procedures such as co-rolling, multi-layer casting, or casting to obtain a controlled gradient of the concentration of an element such as magnesium within the plate thickness. Alloys are chosen and positioned within the plate thickness such that one alloy gives the plate good resistance to perforation and the other gives it good FSP resistance. However, making such panels requires the use of complex and expensive processes.

### SUMMARY

[0012] The applicant attempted to develop a armor shielding system particularly adapted to fast vehicles such as military vehicles, typically on wheels, with better efficiency in terms of AP and FSP protection relative to the transported weight, that is easier to make and less expensive than known products.

[0013] A first purpose of the invention is a armor panel comprising an aluminium alloy plate characterised in that:

[0014] a) said aluminium alloy has the following chemical composition expressed in percentages per weight:

[0015] 5.1%≤Zn≤9.7%

[0016] 1.5%≤Mg≤2.9%

[0017] 1.2%≤Cu≤2.1%

[0018] Si≤0.4%

[0019] Fe≤0.5%

[0020] Mn≤0.3%

[0021] Cr≤0.28%

[0022] Ti≤0.2%

[0023] Zr≤0.15%

[0024] the remainder being aluminium and inevitable impurities, the content by weight of each element being less than 0.05%, and the sum being less than 0.15%;

[0025] b) said plate comprises a face oriented towards the projectiles and a face opposite said face oriented towards projectiles coated with a composite reinforcing layer comprising reinforcing fibres or bands with high mechanical performance that confers a high ballistic protection capability on them. Such reinforcing fibres or bands with a high ballistic protection capability may be made from one or several materials belonging to the group including:

[0026] glass with high mechanical performance such as R, H, S glass or preferably S2 glass;

[0027] aramids, preferably para-aramids such as Kevlar®;

[0028] High Performance PolyEthylenes (HPPE) or Ultra-High Molecular Weight PolyEthylenes (UHMWPE or UHMW), that are strongly oriented polyethylenes in the form of fibres, threads or bands, for example Tensylon®.

### BRIEF DESCRIPTION OF THE DRAWINGS

[0029] FIGS. 1-4 depict embodiments as described herein.

### DETAILED DESCRIPTION OF A PREFERRED EMBODIMENT

[0030] Advantageously, said composite reinforcing layer comprises one or preferably several single-directional or woven fabrics made from threads comprising fibres with a high ballistic protection capability.

[0031] The threads or bands are preferably impregnated with a thermoplastic or thermosetting resin, typically a modified PVB (polyvinyl butyral) phenolic resin. The fabrics may be made by weaving several weaves (single-directional, basket weave, fabric stiffener, etc.). The composite reinforcing coating is obtained for example by stacking the fabrics on each other and then compressing them hot.

[0032] When values or ranges are listed herein, the value itself is included. For example, "more than X" can also include X.

[0033] The term "plate" is used to refer to a flat product that may actually be a sheet or a plate with a thickness of more than 5 mm, preferably more than 20 mm, typically close to 20-30 mm. The width/thickness ratio of the plate is preferably but not necessarily more than 10. The thickness of the composite panel is typically less than 50 mm, preferably less than 40 mm and it has a mass per unit area less than 125 kg/m<sup>2</sup>, preferably less than 110 kg/m<sup>2</sup>, and even more preferably less than 100 kg/m<sup>2</sup>. The advantage of such armor panels is that they provide the best possible AP and FSP protection with the lowest possible mass per unit area. Thus, a composite panel according to the invention has a mass per unit area of less than 90 kg/m<sup>2</sup>, or even less than 85 kg/m<sup>2</sup>, it might also be possible to achieve protection level 5 defined in STANAG 4569 (V50FSP=960 m/s with a 20 mm calibre projectile fired from 25 m).

[0034] The aluminium alloy plate includes one face oriented towards the projectiles that may receive the impact directly, or that on the contrary may be protected for example by ceramic tiles. It includes one face opposite said face oriented towards the projectiles that is covered by a composite reinforcing layer although there is not necessarily a continuous bond over the entire contact surface, for example by means of an adhesive binder. For example, all that is necessary is that the composite reinforcing layer is kept fixed to the plate around the periphery of the plate by gluing or any other attachment means, typically mechanical.

[0035] We carried out AP and FSP tests on aluminium alloy plates coated or not coated with a composite reinforcing layer comprising aramid fibres. AP perforation tests use 7.62 mm calibre and 35.6 mm long projectiles called "0.30 cal AP M2" that have a steel core, an intermediate lead layer and a copper ogive casing. For the panels according to the invention and the panels for which comparative tests were carried out, FSP tests use 23 mm long steel projectiles called "20 mm FSP", the cylindrical part of which is 20 mm in diameter.

[0036] We observed firstly that in the target range of mass per unit area (50 to 125 kg/m<sup>2</sup>), the results of perforation tests on the tested panel structures (plates from 19 to 46 mm thick, panels between 30 and 50 mm thick, ratio of the weight of the composite reinforcing layer/total panel weight less than 25%), depended essentially on the alloy of the plate and the mean mass per unit area of the composite panel: a panel made of a given uncoated alloy gives a result (expressed by the velocity V50) practically identical to the result for a panel composed of the same alloy but thinner and coated with a composite reinforcing layer with a thickness such that the assembly has the same mass per unit area. A slight deteriora-

tion of AP properties was even observed when the ratio by weight of the layer of composite stiffener/total weight of the panel is less than of the order of 22%. Thus, considering only the criterion for resistance to perforation, an uncoated plate has a significant economic advantage and is smaller for exactly the same or even better performance. Among tested materials, aluminium alloys in the 7xxx series give better results than alloys in the 5xxx and 6xxx series and steels for a comparable mass per unit area.

[0037] The results of FSP tests led to a different and surprising finding. The applicant observed that if plates are covered with a composite reinforcing layer comprising reinforcing fibres or bands with a high ballistic protection capability, for example made of aramid fibres, with a mass per unit area more than 0.5 kg/m<sup>2</sup>, preferably 1 kg/m<sup>2</sup>, and even more preferably 2 kg/m<sup>2</sup>, the gain in terms of an increase in V50 as a function of the increase in the mass per unit area of the armor panel, is significantly more for aluminium alloys and particularly for alloys in the 7xxx series.

[0038] However, the best AP-FSP compromise is obtained with alloys in the 7xxx series that have a sufficiently high content of zinc and copper. Thus 7039 and 7020, if they are present, associated with a composite reinforcing layer of aramid fibres, have significantly improved FSP performances, but have a relatively poor performance in AP perforation tests.

[0039] Thus, the alloy for the plate according to the invention has the following composition, in which contents are expressed in percentages by weight:

- [0040] 5.1%≤Zn≤9.7% preferably 7.5%≤Zn≤8.7%.
- [0041] 1.5%≤Mg≤2.9% preferably 1.8%≤Mg≤2.7%.
- [0042] 1.2%≤Cu≤2.1% preferably 1.4%≤Cu≤2.1%
- [0043] Si≤0.4% preferably Si≤0.12%
- [0044] Fe≤0.5% preferably Fe≤0.15%
- [0045] Mn≤0.3% preferably Mn≤0.2%
- [0046] Cr≤0.28% preferably Cr≤0.05%
- [0047] Ti≤0.2% preferably Ti≤0.05%
- [0048] Zr≤0.15% preferably Zr≤0.05%
- [0049] other elements≤0.05% individually and≤0.15% total.

[0050] Preferably, these alloys are treated to obtain a state not only with high instantaneous mechanical properties (strength UTS, conventional yield stress TYS, elongation at failure E %) but also good toughness. Advantageously, a solution treatment will be carried out followed by quenching and annealing to obtain states such as T6 (maximum UTS), T64 (quenched slightly under-annealed state), or preferably T651 (relaxed quenched by controlled moderate tension and annealing) or even T7651 (relaxed quenched by controlled moderate tension and over-annealing).

[0051] In practice, the mass per unit area of the composite reinforcing layer is between 2 and 25 kg/m<sup>2</sup>. It is preferably less than 20 kg/m<sup>2</sup>, even more preferably less than 15 kg/m<sup>2</sup> mainly due to the cost.

[0052] The effect of this composite reinforcing layer on improvement of FSP properties is certainly more accentuated when the mass per unit area of the composite reinforcing layer is high, but it is remarkable that this effect that becomes manifest with aluminium alloy plates, particularly plates composed of the alloy according to the invention, even if the composite reinforcing layer is thin with a mass per unit area of the order of 1 kg/m<sup>2</sup>, in other words as soon as the panel is coated with three or four woven aramid fabrics.

[0053] When the mass per unit area is less than 90 kg/m<sup>2</sup>, aluminium alloys such as 7xxx have FSP performances lower

than the performances of a steel for armor shielding, such as HHS ("high hardness steel"). But when these alloys are combined with a composite reinforcing layer comprising aramid fibres, the FSP results are quickly better than the results for steel, even if the steel is covered with the same type of composite reinforcing layer with a comparable mass per unit area. For example, to obtain the same improvement of FSP performances on a steel plate as is observed on 7xxx plates with a composite reinforcing layer with a mass per unit area equal to only 2 kg/m<sup>2</sup>, said steel plate needs to be associated with a composite reinforcing layer between 4 and 6 times thicker, all other things being equal.

[0054] The effect of the composite reinforcing layer on the improvement of FSP properties is particularly remarkable when the plate is 7449 T651.

[0055] Among the different tested composite reinforcing layers, the layer composed of a stack of woven fabrics using Kevlar® 129 threads gave good results regardless of the type of weaving made. Kevlar® 129 grade is known for its lightweight and its high mechanical performances and particularly its high toughness.

[0056] 7449 T651 plates covered with fabric layers woven from Kevlar® 129 threads have the best AP and FSP performances. This alloy can give a V50 for the FSP test greater than 950 m/s with an armor panel for which the global mass per unit area is less than 95 kg/m<sup>2</sup>, or even less than 90 kg/m<sup>2</sup>.

[0057] FIG. 1 shows the results of AP tests carried out on shielding panels composed of metal plates coated or not coated with a composite reinforcing layer comprising aramid fibres.

[0058] FIG. 2 shows the results of FSP tests carried out on armor panels composed of aluminium alloy plates in the 7xxx series and made of steel, coated or not coated with a composite reinforcing layer comprising aramid fibres.

[0059] FIG. 3 shows the improvement of FSP properties in terms of relative variation of V50 as a function of the increase in mass per unit area, for several materials.

[0060] FIG. 4 shows the improvement of FSP properties in terms of an improvement of V50 as a function of the increase in mass per unit area due to the composite reinforcing layer, for several materials.

#### EXAMPLE

[0061] Armor plates were made from thick plates made of different alloys. They were machined to different thicknesses between 25 and 40 mm. Table 1 shows the main constituents of their chemical compositions.

TABLE 1

Alloy	Type	Si	Fe	Cu	Mg	Zn
A	7449	0.05	0.07	1.9	2.1	8.5
B	6061	0.62	0.4	0.26	1.0	0.00
C	7020	0.13	0.12	0.13	1.22	4.69
D		0.05	0.07	1.7	2.0	9.4

[0062] Table 2 shows the state, thickness and average mechanical properties of these plates (tension, transverse longitudinal direction).

TABLE 2

Alloy	State	Thickness	Rp0.2 (MPa)	Rm (MPa)	A %
A	T651	30	583	651	11
B	T6	30	295	330	12
C	T651	30	360	420	12
D	SHT 472° C.- quenched-6 h 120° C. + 7 h 135° C.	25	694	707	11.5

[0063] Some plates were covered with a composite reinforcing layer comprising a stack of a various number of fabrics woven in threads based on Kevlar® 129 fibres with a linear density of 1330 dtex, coated with polyvinyl butiral (PVB) resin, each fabric having a mass per unit area of about 275 g/m<sup>2</sup>. Composite reinforcing layers with different thicknesses were made by stacking a variable number of fabrics, and the stack was then hot compressed in a press.

[0064] Ballistic perforation tests ("AP tests") Table 3 contains the results of "0.30 cal AP M2" tests carried out on thick plates coated or not coated with a composite reinforcing layer. When there was a composite reinforcing layer, it was placed on the side opposite the projectile. The mass per unit area of the stack of fabrics woven from Kevlar® 129 threads is given in the fourth column in table 3 below.

[0065] FIG. 1 shows the different results obtained and compares them with results known on other materials (5083 H131 (MIL-DTL-46027); RHA Steel (MIL-A-12560); 7039 T64 (MIL-DTL-46063), 6061 T651 (MIL-DTL-32262)).

[0066] It is found that for masses per unit area typically less than 100 kg/m<sup>2</sup>, the performances of 5083 and 6061 alloys are not as good as the performances of steels such as RHA Steel, which has a lower performance than 7449. AP performances of 7039 plates relative to the mass per unit area are hardly better than steel and significantly lower than 7449. Known AP tests on the 7020 alloy were made with a different projectile and the results are not directly comparable. However, they show that the AP performances of 7020 are not better and are rather worse than the results of 7039.

[0067] Once the thick 7449 plates have been coated with woven fabric made of Kevlar® 129 threads, their behaviour is similar or slightly less good than uncoated thick plates, for equal mass per unit area.

TABLE 3

Test piece	Alloy	Thickness (mm)	Stack of layers woven from Kevlar® 129 threads			V50 (m/s)
			Mass per unit area (kg/m <sup>2</sup> )	Glue	Mass per unit area (kg/m <sup>2</sup> )	
1-1	7449 T651	30	0	0	85.5	805
1-2	7449 T651	30	0	0	85.5	815
1-3	7449 T651	30	16.7	1	102	862
1-4	7449 T651	30	10.7	1	96	844
1-5	7449 T651	30	10.7	0	96	845
1-6	7449 T651	30	22.9	0	108	876
1-7	7449 T651	39.3	0	0	112	948
1-8	7449 T651	39.9	0	0	114	944
1-9	7449 T651	39.9	0	0	114	936
1-10	7449 T651	39.9	0	0	114	877
1-11	7449 T651	25.5	0	0	73	724
1-12	7449 T651	19	0	0	55	612
1-13	6061 T6	30	0	0	81	641

TABLE 3-continued

Test piece	Alloy	Thickness (mm)	Stack of layers woven from Kevlar® 129 threads		Mass per unit area (kg/m²)	Glue	Mass per unit area (kg/m²)	V50 (m/s)
			Mass per unit area (kg/m²)	Glue				
1-14	6061 T6	30	16.7	1	98		702	
1-15	6061 T6	30	22.9	1	104		767	

## FSP Tests

[0068] Table 4 contains the results of the “20 mm FSP” tests carried out on thick plates coated or not coated with a composite reinforcing layer. When there was a composite reinforcing layer, it was placed on the face opposite the face that will receive the impact of the projectile.

[0069] FIG. 2 shows the different results obtained on 7020, 7449 and a high hardness steel (HHS) with a Brinell hardness of between 420 and 480 HB. These results are compared with the results obtained on other materials (7039 T64 (MIL-DTL-46063), RHA Steel (MIL-A-12560)). FIG. 2 also compares the results obtained for coated and uncoated 7xxx plates, and coated and uncoated steel plates.

[0070] FIG. 2 shows that the performance of uncoated steel plates is higher for FSP tests than aluminium alloy plates, as long as the mass per unit area remains less than about 100 kg/m<sup>2</sup>.

TABLE 4

Test piece	Alloy	Thickness (mm)	Composite reinforcing layer		Mass per unit area (kg/m²)	Glue	Mass per unit area	V50 (m/s)
			Mass per unit area (kg/m²)	Glue				
2-1	7449 T651	30	0	0	85.5		534	
2-2	7449 T651	39.3	0	0	112		827	
2-3	7449 T651	39.9	0	0	114		842	
2-4	7449 T651	39.9	0	0	114		884	
2-5	7449 T651	39.9	0	0	114		877	
2-6	7449 T651	30	3.9	1	89.4		837	
2-7	7449 T651	30	7.7	1	93.2		942	
2-8	7449 T651	30.8	10.7	1	98.5		1102	
2-9	7020 T651	28.5	0	0	79.1		534	
2-10	7020 T651	30.75	0	0	85.3		600	
2-11	7020 T651	30.75	3.9	1	89.2		834	
2-12	HHS	10	10.7	1	89.3		812	
2-13	HHS	10	0	0	78.6		585	

[0071] Experimental points obtained with uncoated 7449 T651 show a trend curve parallel to curve for 7039 T64, but with slightly lower FSP performances. Experimental points obtained with 7020 T651 are also on a trend curve approximately parallel to the curve for 7039 T64 but with slightly higher FSP performances. The experimental point of uncoated HHS steel plate is slightly below the trend curve for “RHA Steel”.

[0072] Points for 7449 T651 plates coated with a composite reinforcing layer comprising aramid fibres are significantly higher than the curve that contains the FSP results for uncoated plates. The difference, significant even with a thin coat, is greater when the composite reinforcing layer is thicker. Thus, the combination of a 7449 T651 plate with a composite reinforcing layer comprising Kevlar® 129 fibres with a mass per unit area of 10.7 kg/m<sup>2</sup> can give a V50 of more than 1100 m/s

[0073] The results for the coated 7020 T651 plate also show the significant influence of the composite reinforcing layer. This appears nevertheless lower than that observed on 7449 plates. Furthermore, known AP results on the 7020 alloy suggest that alloys with low copper content such as 7020 and 7039, even associated with a composite reinforcing layer comprising aramid fibres, cannot give a good AP-FSP compromise.

[0074] The FSP results for the coated steel plate also show an influence of the composite reinforcing layer, but this is significantly lower.

[0075] Table 5 shows FSP results on coated aluminium alloy plates and estimates the gains obtained in comparison with uncoated plates. For each composite panel, the 6<sup>th</sup> column contains the results obtained for the uncoated plate A composed of the same material as the core of the composite panel and with the same thickness as the composite panel, and the 7<sup>th</sup> column contains estimated values for an uncoated plate B composed of the same material as the core of the composite panel and with the same mass per unit area as the composite panel. It can be seen that the gain due to the presence of the composite reinforcing layer expressed in terms of an increase of V50, is higher by a factor of between 4.8 and 7.8 for aluminium alloys. This coefficient is of the order of 6.6 for aluminium alloy and only of 4.5 for steel, for the same thickness of the composite reinforcing layer.

[0076] FIG. 3 shows these same results in the form of a relative increase in V50 as a function of the relative increase in the mass per unit area. Thick curves are associated with 7449. Curve (I), that is approximately straight and has a low gradient, represents the effect of the increase in the thickness of uncoated plates on the relative increase of V50. Curve (II) shows the effect of increasing the thickness of the composite reinforcing layer in the composite panels on the relative increase of V50.

TABLE 5

Test piece	Core thickness (mm)	Panel mass per unit area (kg/m²)	Core mass per unit area (kg/m²)		V50 A (m/s)	V50 B (m/s)	Gain V50 B - A (m/s)	Gain V50 Composite-A (m/s)	Factor
			V50 (m/s)	area (kg/m²)					
2-6	30	89.4	837	85.5	534	577	43	303	7.0
2-7	30	93.2	942	85.5	534	620	86	408	4.8
2-8	30.8	98.5	1102	87.8	603	679	76	499	6.6
2-11	30.8	89.2	834	85.3	600	641	41	234	5.7
2-13	10	89.3	812	78.6	585	635	50	227	4.5

[0077] For example, it can be seen in FIG. 3 that a relative increase of 10% in the mass per unit area of the 7449 T651 armor panel, leads to a relative increase in FSP performances of the order of 20% if all that is done is to increase the panel thickness, and of the order of 80% if a composite reinforcing layer comprising aramid fibres is associated with it. The FSP performances of composite panels with a 7020 core are also significant. Performances are more modest when the panel core is made of steel (dashed lines curve).

[0078] FIG. 4 shows the gain in V50 as a function of the increase in mass per unit area. The effect of the composite reinforcing layer on the improvement of FSP properties is very clear even if the composite reinforcing layer is thin, once the mass per unit area of said composite reinforcing layer is greater than a value of the order of 1 kg/m<sup>2</sup>, which typically corresponds to a stack of at least five fabrics woven from aramid thread. It can also be seen that to obtain the same improvement in FSP performances as is observed in 7xxx plates with a composite reinforcing layer with a mass per unit area equal to only 2 kg/m<sup>2</sup> on a steel plate, said steel plate must be associated with a composite reinforcing layer between 4 and 6 times thicker, all other things being equal.

[0079] Finally, an analysis of the results leads to the conclusion that protection level 5 as defined in standard STANAG 4569 [V50 greater than 960 m/s for 20 mm FSP tests] can be obtained with a composite panel made of an aluminium alloy with the composition coated by a composite reinforcing layer containing aramid fibres with a mass per unit area of less than 95 kg/m<sup>2</sup>.

1. Armor panel comprising an aluminium alloy plate wherein:

a) said aluminium alloy has the following chemical composition expressed in percentages per weight:

5.1%≤Zn≤9.7%

1.5%≤Mg≤2.9%

1.2%≤Cu≤2.1%

Si≤0.4%

Fe≤0.5%

Mn≤0.3%

Cr≤0.28%

Ti≤0.2%

Zr≤0.15%

b) said plate comprises a face adapted to be oriented towards a projectile and a face opposite said face adapted to be oriented towards a projectile coated with a composite reinforcing layer comprising reinforcing fibres or bands with high mechanical performance that confers a high ballistic protection capability on them.

2. Armor panel according to claim 1, wherein the reinforcing fibres or bands with a high ballistic protection capability may be made from one or more materials selected from the group consisting of:

glass with high mechanical performance optionally R, H, S

glass or optionally S2 glass;

aramids, optionally para-aramids;

High Performance PolyEthylenes (HPPE) or Ultra-High Molecular Weight PolyEthylenes (UHMWPE or UHMW).

3. Armor panel according to claim 1, wherein said composite reinforcing layer comprises one or optionally more single-directional or woven fabrics made from threads comprising fibres with a high ballistic protection capability.

4. Armor panel according to claim 3 in which said composite reinforcing layer comprises fabric woven from para-aramid threads impregnated with resin.

5. Armor panel according to claim 4, in which said resin is a modified PVB (polyvinyl butyral) phenolic resin.

6. Armor panel according to claim 1, in which the composite reinforcing layer is a stack of hot compressed fabrics.

7. Armor panel according to claim 1, having a thickness of at least 5 mm and at most 50 mm and a mass per unit area of at most 125 kg/m<sup>2</sup>.

8. Armor panel according to claim 7, having a thickness of at least 20 mm and at most 40 mm and a mass per unit area of at most 110 kg/m<sup>2</sup>, and optionally at most 100 kg/m<sup>2</sup>.

9. Armor panel according to claim 1, wherein the mass per unit area of the composite reinforcing layer comprising aramid fibres represents not more than 25%, optionally not more than 15% of the total mass per unit area of the panel.

10. Armor panel according to claim 1, wherein the mass per unit area of the composite reinforcing layer comprising aramid fibres is at least 0.5 kg/m<sup>2</sup>, optionally 1 kg/m<sup>2</sup>, and/or optionally 2 kg/m<sup>2</sup>.

11. Armor panel according to claim 1, wherein mass per unit area of the composite reinforcing layer comprising aramid fibres is at most 25 kg/m<sup>2</sup>, optionally 20 kg/m<sup>2</sup>, and/or optionally 15 kg/m<sup>2</sup>.

12. Armor panel according to claim 1, wherein said plate is made from 7449 alloy, optionally in T651 state.

13. Armor panel according to claim 1, wherein said composite reinforcing layer comprises one or more woven fabrics using Kevlar® 129 coated with polyvinyl butyral (PVB) resin.

\* \* \* \* \*



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(54) **MULTI-LAYER NON - WOVEN FABRIC  
MULTI-USE MATERIAL FOR BALLISTIC  
AND STAB RESISTANCE COMPRISING  
IMPREGNATED AND ORIENTED FIBER NON  
- WOVEN FABRIC LAYERS;  
MANUFACTURING, METHOD, AND  
PROTECTION GARMENT PRODUCED  
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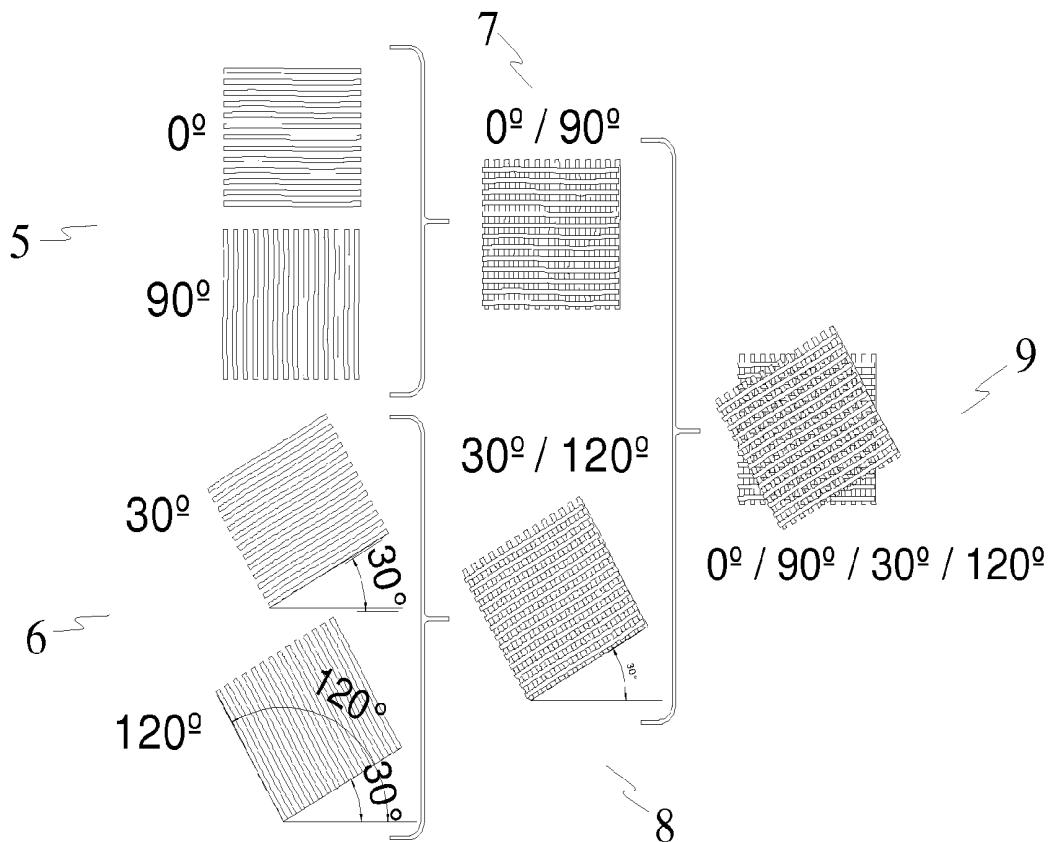
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(57) **ABSTRACT**

Multi-layer non-woven fabric material composed of non-woven fiber sheets of aramide/polyethylene fibers, impregnated with resin and/or a filler material, and oriented at various angles, which is used for manufacturing protection garments. The invention also describes a method for manufacturing said multi-layer non-woven fabric material and the protection garments thus obtained.



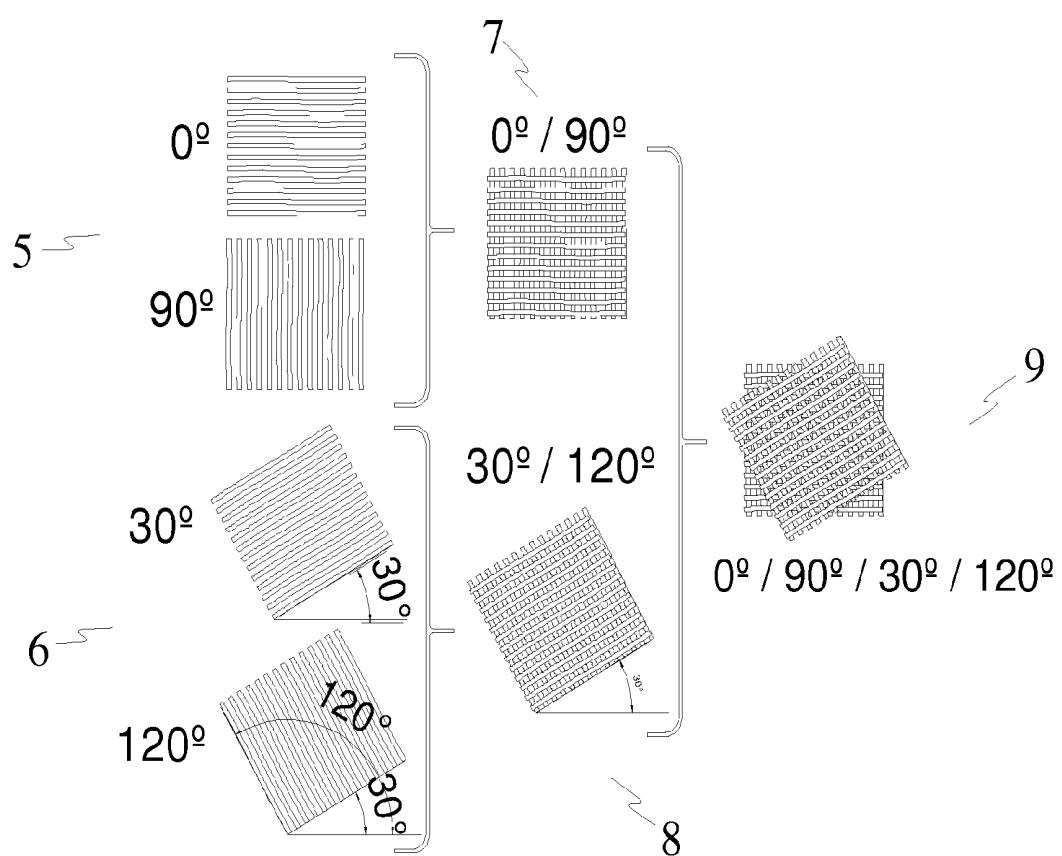


Fig. 1

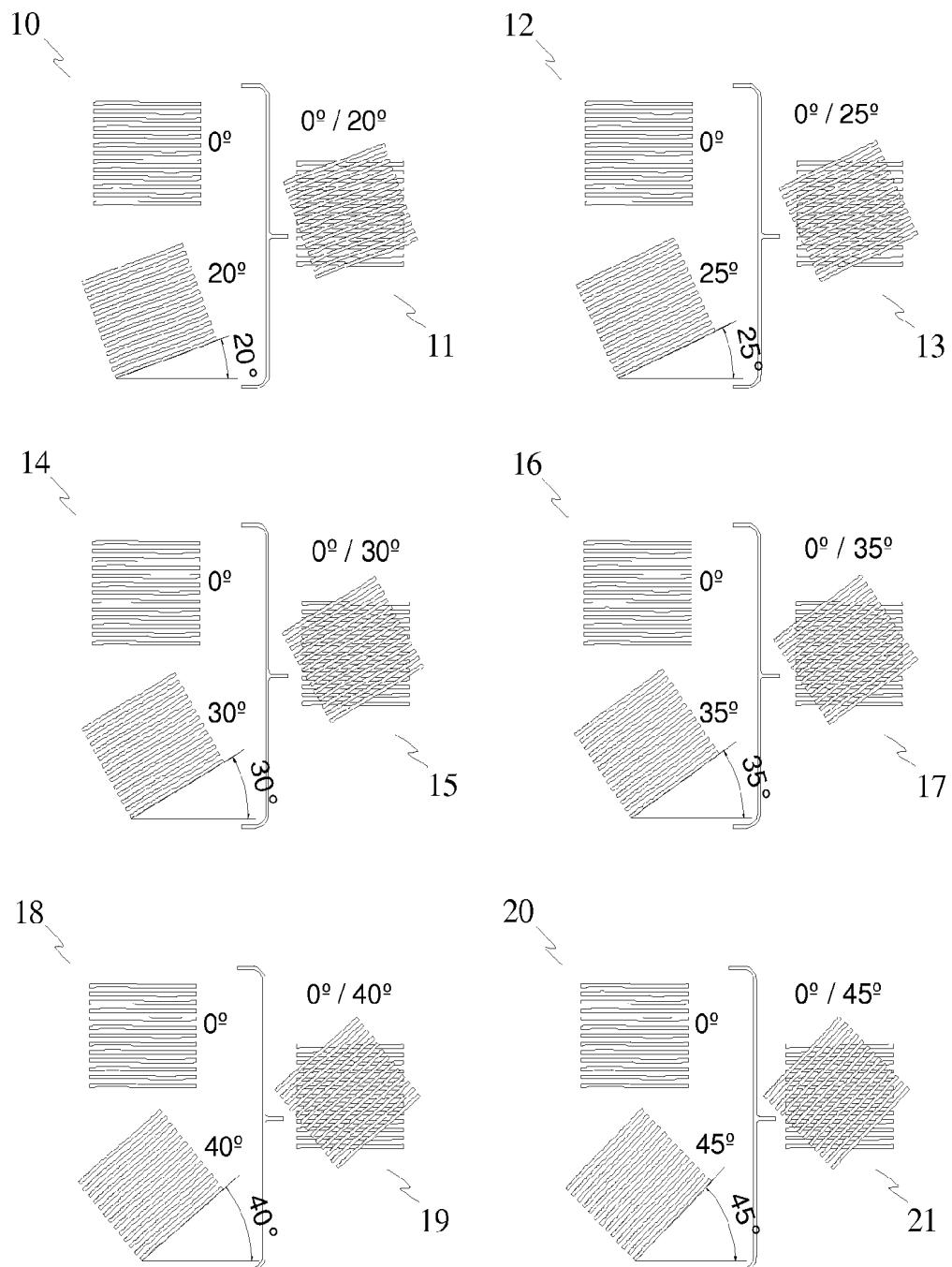


Fig. 2

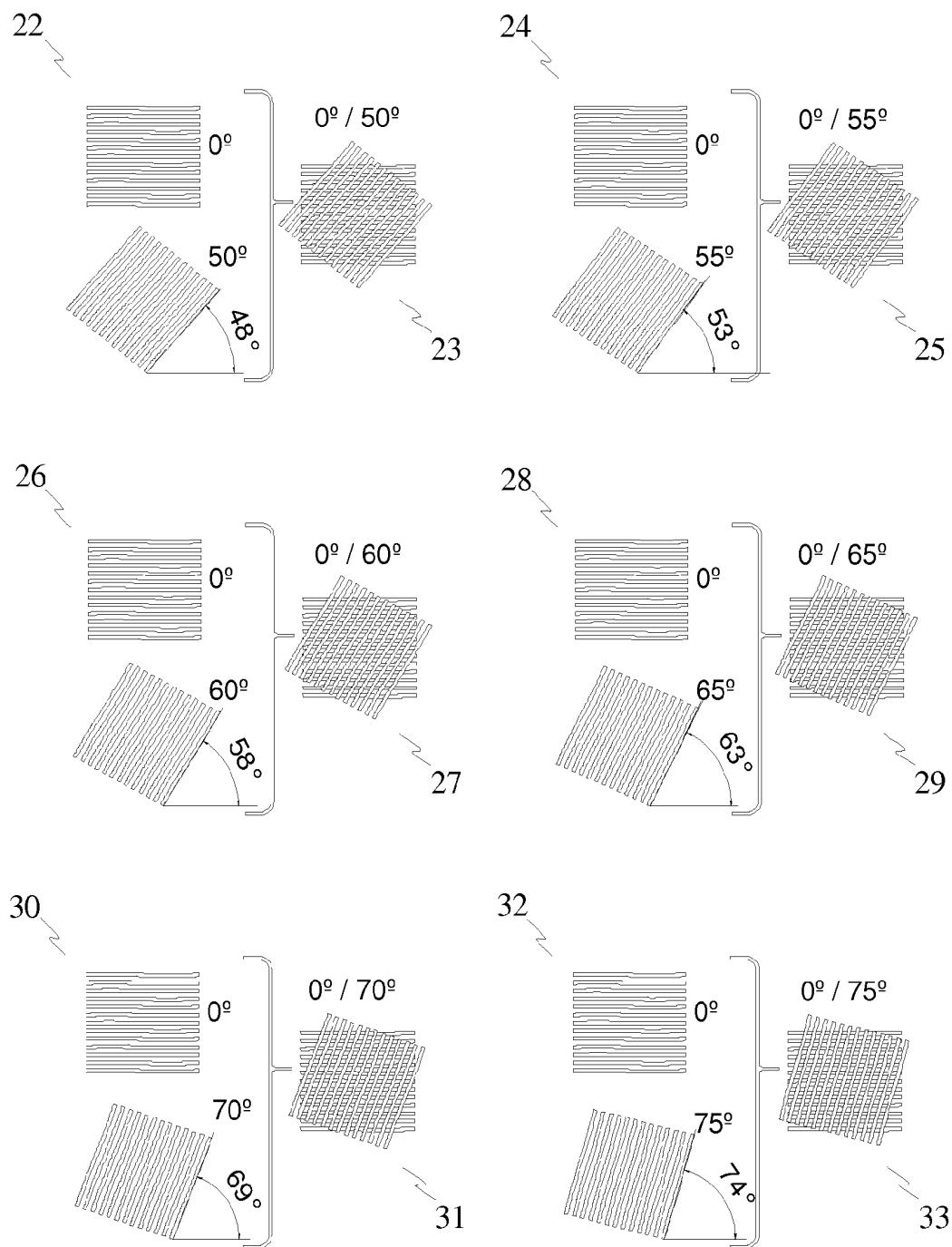


Fig. 3

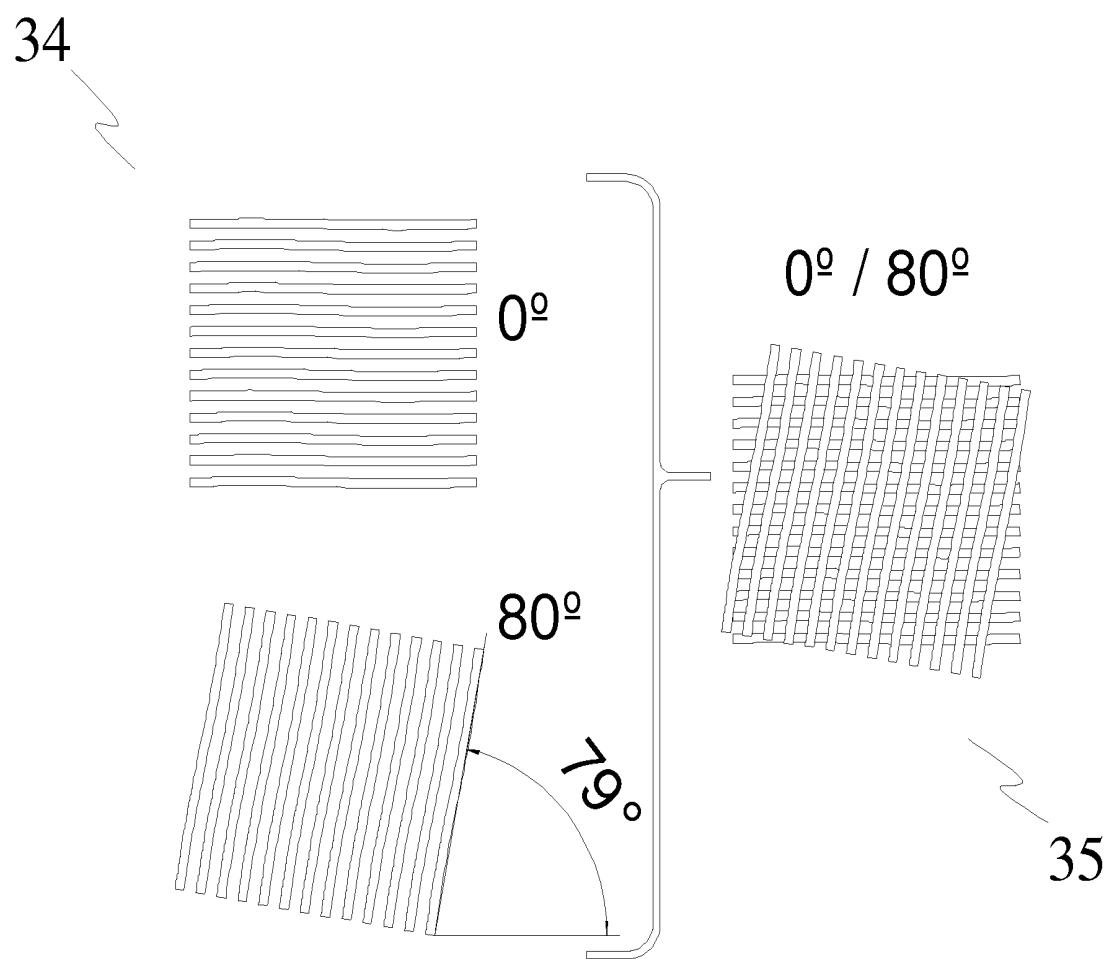


Fig. 4

**MULTI-LAYER NON - WOVEN FABRIC  
MULTI-USE MATERIAL FOR BALLISTIC  
AND STAB RESISTANCE COMPRISING  
IMPREGNATED AND ORIENTED FIBER NON  
- WOVEN FABRIC LAYERS;  
MANUFACTURING, METHOD, AND  
PROTECTION GARMENT PRODUCED  
THEREBY**

CROSS-REFERENCES

[0001] None

GOVERNMENT RIGHTS

[0002] None

OTHER PUBLICATIONS

[0003] None

BACKGROUND OF INVENTION

[0004] 1. Field of Invention

[0005] The present invention relates to a multi-layer anti-trauma material composed of non-woven fabrics made of impregnated fibers oriented at specific angles, impregnated with a resin and/or filler material. Said material is used in the manufacture of multi-threat body armors, for example vests and any other kind of garment, which are shrapnel-proof, stab-proof and against the penetration of piercing and cutting objects.

[0006] 2. Description of the Related Art

[0007] In order to provide personal protection against projectiles or piercing objects, special fabrics or layers are used for the manufacture of body armors, vests, helmets, shields and any kind of safety and protection garment, for both industrial and sports purposes. Said layers and fabrics can be manufactured from fibers such as aramide, high molecular weight polyethylene and polybenzazoles. Said materials are disclosed in, for example, U.S. Pat. No. 7,073,538B2 to Bhatnagar published on Jul. 11, 2006, U.S. Pat. No. 7,288,307B2 to Bhatnagar published on Oct. 30, 2007, US 2001/0053645A1 to Henderson published on Dec. 20, 2001, US 2006/0121805A1 to Krulic published on Jun. 8, 2006, and in the International Patent Application PCT WO 2008/101138A1 to Bhatnagar, published on Aug. 21, 2008 as well as in Patent ES 2187013.

[0008] Said articles exhibit various degrees of resistance against the penetration of knives and in general of projectiles of any kind. High-strength fibers made of Ultra High Molecular Weight Polyethylene (UHMW PE), aramides and polybenzazoles are incorporated into these materials under various forms, either as hybrid compositions (mixtures of polyethylene and aramides, woven or non woven), rigid compositions (prepared by bonding of fabric layers under pressure) or flexible compositions. Fibers in a non-woven layer can be oriented in a single direction 0°/90°, typically containing a matrix resin to stabilize the structure.

[0009] Another known procedure comprises rotating the fabrics so that they will bear an angular relation of 0°/90° or 0°/45°/90°/45°/90° to each other, or in different angles, for the purpose of constructing rigid or moderately flexible materials, by bonding fabric layers under heat and pressure, so that the matrixes of individual layers become bonded into a single composite matrix of high mechanical strength, suitable for construction. The material thus obtained is characterized by

such rigidity that, although it can be used with excellent results in armored structures, it is difficult to use in body armors, due to its limited flexibility.

[0010] The aforementioned references have several disadvantages. Those include inflexibility of the final product whether woven or non woven, increased weight of the product to adequately resist both projectile and piercing objects, inability to properly disperse impact energy so as to minimize trauma in its application to a vest type body armor. A need exists to provide low cost, low weight multi-threat body armor which is shrapnel-proof, stab-proof and can protect against the penetration of piercing and cutting objects. As such none of the above references discloses a material such as the one disclosed in the present invention. Therefore it is the object of this invention to solve one or more of these problems.

SUMMARY OF INVENTION

[0011] In a first embodiment, the object of the invention comprises a non-woven/UD band comprised by a first set of unidirectional, continuous threads/filaments, laid down in a first plane of UHMWPE 1000 and a second set of unidirectional continuous threads/filaments on top of said first plane laid down transversely in different angles to the first set of threads. By applying different information techniques, the drawing ratio (% elongation at break), ASTM D-638 and DIN 53455 in a percentage value of UHMW/PE 1000 of 350, as well as the elasticity module (kg/cm<sup>2</sup> tension) ASTM D-638 and DIN 53457 in a tension value of UHMW/PE 1000 of 6000 may be achieved.

[0012] In the case of aramid fibers made up from aromatic polyamides filed in U.S. Pat. No. 3,671,542, with different formulas, will give a tenacity of 23 g/denier, 203 cN/tex/424000 psi, 2920 Mpa, 1500 denier/1670 dtex.

[0013] For example, poly(p-phenylene terephthalamide), filament's produced by DuPont®, under the trademark KEVLAR® used in the formation of different composites resistant to ballistic impact and whose commercial denomination is KEVLAR® 29/129 are compatible for use in this invention. Also, the poly(m-phenylene isophthalamide) fibers (whose commercial denomination is NOMEX®) produced by DuPont® are also compatible for this invention.

[0014] In accordance with the teachings of this invention as embodied and described herein, an improved multi-layer non-woven fabric material composed of multiple non-woven fabric layers or laminates each made up of individually impregnated unidirectional fiber sheets and superimposed so that the fibers in each layer of non-woven fabric form various angles of 0° to 90°, including but not limited to 20°, 25°, 30°, 35°, 40°, 45°, 50°, 55°, 60°, 65°, 70°, 75°, 80°, and 90° and so on with the fibers of the adjacent layer or non-woven fabric. Each layer is impregnated with a resin and/or filler material. As many non-woven fabric layers as desired can be superimposed, depending on the intended purpose of the material. The superimposed non-woven fabric layers are not bonded or glued together only joined at the ends; therefore a flexible material is obtained, ideally suited for its use in garments. The protection garments manufactured with the multi-layer non-woven fabric material of the invention, in addition to having greater flexibility, achieve an optimum resistance to penetration by projectiles, and also, most remarkably, are more resistant to penetration by piercing objects than the state-of-the-art materials.

[0015] The present invention, which comprises non-woven fabric layers individually impregnated with a resin material. Each non-woven fabric layer is superimposed so that the fibers in each layer form angles of 0°/90°, 0°/20°, 0°/25°, 0°/30°, 0°/35°, 0°/40°, 0°/45°, 0°/50°, 0°/55°, 0°/60°, 0°/65°, 0°/70°, 0°/75°, 0°/80° with the fibers of the adjacent layer. As many non-woven fabric layers as desired can be superimposed, depending on the intended purpose of the material (i.e. fewer layers for flexibility and more layers for rigidity). The superimposed non-woven fabric layers are not bonded or glued together; therefore a flexible material is obtained, ideally suited for its use in garments. The protection garments manufactured with the multi-layer non-woven fabric material of the invention, in addition to having greater flexibility, achieve an optimum resistance to penetration by projectiles, and also, most remarkably, (due to the incorporation of the resin impregnation) are more resistant to penetration by piercing objects than the state-of-the-art materials.

[0016] It is evident that the multi-axial band of the invention may be composed of a larger quantity of intermediate planes and/or different rotation angles between the planes of yarns which are illustrated in the figures. For the purposes of this invention, the fiber is dimensionally elongated in its length, being larger than the width transversal dimensions. Consequently, the fiber term includes fiber filaments, regular or the irregular to the transversal section of different angles.

[0017] A thread is a continuous strand composed by many fibers or filaments. The fibers making up the thread may be continuous along the length of the thread or fibers. The threads of unidirectional continuous filaments are the main structural components of the unidirectional band in different multi-axial angles of the invention. The threads of unidirectional continuous filaments may be incorporated the material in different fibers independently formed in groups by: polyolefins of high molecular weight, aramids, polybenzazoles and/or a mixture thereof.

[0018] A first object of the present invention is to provide a multi-layer non-woven fabric material composed of multiple flexible non-woven fabric layers or laminates made of oriented unidirectional fiber sheets wherein said non-woven fabric layers are superimposed so that the fiber in one non-woven fabric sheet form a certain angle with the fibers in adjacent non-woven fabric sheets.

[0019] A second object of the present invention is to provide a flexible multi-layer non-woven fabric material wherein the non-woven fabric layers made of oriented unidirectional fiber sheets are impregnated with a resin.

[0020] A third object of the present invention is to provide a flexible multi-layer non-woven fabric material wherein the non-woven fabric layers made of oriented unidirectional fiber sheets are impregnated with a resin as well as a filler material.

[0021] A fourth object of the present invention is the use of the multi-layer non-woven fabric material to make body armors or other protection and security garments and elements with substantially reduced weight over that currently available in the prior art.

[0022] A fifth object of the present invention is to provide a method for manufacturing the flexible material disclosed herein.

#### BRIEF DESCRIPTION OF DRAWINGS

[0023] FIG. 1 is a top perspective view of the non-woven multi-layered non-woven fabric manufacture, at 0°/90°, and 30°/120°.

[0024] FIG. 2 is a top perspective view of the non-woven fabric layer or laminate manufacture, at 0°/20°, 0°/25°, 0°/30°, 0°/35°, 0°/40°, and 0°/45°.

[0025] FIG. 3 is a top perspective view of the non-woven fabric layer or laminate manufacture, at 0°/50°, 0°/55°, 0°/60°, 0°/65°, 0°/70°, and 0°/75°.

[0026] FIG. 4 is a top perspective view of the non-woven fabric layer or laminate manufacture, at 0°/80°.

#### DETAILED DESCRIPTION OF THE INVENTION

[0027] It is defined here that fiber is to be understood to mean a longitudinally extended series of filaments, microfilaments, ribbons, threads, strips, films, or the like having a regular or irregular cross section with the length of said fiber being substantially longer than the width and thickness. It is also to be understood that a prepreg, fiber sheet, or unidirectional fiber sheet refers to that which is being constructed from a series of parallel fibers joined together through gluing and possibly to be pre-impregnated with a resin. The majority of the fibers comprising the matrix structure are to be parallel to each other. The matrix, matrix composite, laminate, or non-woven fabric layer structure disclosed is the joining of two or more different fiber sheets through varying angles. Finally a multi-layer non-woven fabric is to be understood to mean the non adhesive joining of the ends of two or more non-woven fabric layers through varying angles.

[0028] In one of its preferred embodiments, the material of the present invention is prepared with non-woven fabrics or aramide/polyethylene fiber sheets supplied in rolls called "prepreg", which are slightly pre-impregnated with a resin, to consolidate the structure of the fiber non-woven fabric at 0°/90°, thus providing it sufficient consistency to be unrolled for handling purposes. Even though the objects of the invention could be achieved with any kind of fiber sheet, as long as said fiber sheet meets the above-mentioned specifications, the fiber sheet used for the invention may be, without limitation, any of the fiber sheets or composites marketed world-wide by the Honeywell company under the trade names GoldShield® GV 2112/GN 2115/GN 2117/GN 2118/GV 2018, Spectra Shield® SR 1214/SRII 3124 y SRII 3130.

[0029] To said non-woven prepreg fiber sheet, resins selected from products in thermally stable laminates, amines, cyanates, epoxies, phenolics, non-saturated polyesters, bismaleimides, polyurethanes, silicones, esters, vinyls and their copolymers and mixtures thereof are incorporated by impregnation under high pressure. Polyurethane resins are particularly preferred. Some trade names of preferred resins are, for example, Baycoll® AS 2060, Desmudur® L 75, Desmophen® 1150 and Desmodur® N75 MPA/BA resins from the Bayer Company, and preferentially the Resinex® 4 resin.

[0030] As mentioned above, such chemical compounds (resins) are in general terms applicable to non-woven fabrics. However, different resins provide different advantages and results according to specific goals. Resinex® 4 resin performs best for the purposes of the present invention. The impregnation is carried out in a continuous process, under pressures in the range of 100 psi to 1900 psi (6.89 to 131 bars) and at temperatures between 120 and 145°C. (248 and 293°F.). The roll of non-woven fabric is impregnated and later air-dried at elevated temperature.

[0031] The features of Resinex® 4 resin are set forth below

Properties	Resin	Hardener
Appearance	Black liquid	Brown liquid
Viscosity (at 20° C.)	3500-5500 mPas	100-250 mPas
Specific Gravity (at 20° C.)	1.31	1.24
Flash Point	>200° C.	>200° C.

Properties of the mixture	Test parameters
Mixture Ratio (by weight)	100 resin/25 hardener
Gel Time (at 20° C.)	30-50 minutes
Curing Time (at 20° C.)	24 hours

Properties of the cured mixture	Test parameters
Specific Gravity	1.29
Hardness (Shore A)	92
Tensile Strength	570 psi
Volume shrinkage after curing	2%
Electric Resistance	11 kV/mm
Thermal Conductivity 20-100° C.	0.4-0.5 W/mK
Water Absorption	0.15-0.2%

[0032] Impregnation of the prepreg with resins causes the microfilaments of threads or aramidic/polyolefin fibers to stick together even more, thus giving the non-woven fabric sheet and thus the non-woven fabric a better structure and obtaining a better control of the displacement of each microfilament in the laminar assembly of the non-woven fabric's general structure. The resin incorporated into the fiber sheet by impregnation will bond neighboring filaments all over the fiber sheet area, thus preventing them from displacing when the non-woven fabric is penetrated by a piercing or cutting object. In non-woven fabrics of the prior art, the microfilaments of the fibers would displace or be pushed apart, thus allowing any piercing object such as for example a hypodermic syringe to penetrate.

[0033] By forming such kind of structure, comprising thread microfibers and impregnating resins binding them, the threads are locked in position and their displacement with respect to their normal orientation angle 0°/90° in non-woven fabrics is reduced by 50% when a projectile or cutting/piercing object penetrates the non-woven fabric, by considerably dissipating its kinetic energy. A completely different result is obtained than with a non-impregnated non-woven fabric.

[0034] None of the fabrics of the prior art contains resins as those specified hereinbefore, which differ from those used in pre-impregnation or "prepreg", so to give the non-woven fabric a structure with a high anti-trauma performance compliant with II-A-II-III-A levels of NIJ 0101.06 Standard for body armors, and a performance against the penetration of piercing-cutting objects exceeding levels 1, 2 and 3/Spike/P1 and S1 of the NH 0115.00 Standard.

[0035] In a second embodiment, in addition to impregnating the non-woven fabric sheets with resins as described above, a filler material can be added thereto. The purpose of this procedure is to obtain a better structured material, resistant to piercing objects. The addition is carried out by adding

a particulate material selected, without limitation, from the group comprising aluminum oxide, titanium oxide, carbon/boron oxide, silicon oxide, silicon dioxide, quartz oxide, silicon carbide, titanium carbide, hard glass, etc. In a preferred embodiment, the particulate material used is SiO<sub>2</sub>. The addition of said particulate material or filler material can be carried out together with the impregnation with resin and before cutting the layers for the manufacture of for example, the body armors, or else can be added after cutting the layers for their intended purpose. The pre-impregnated non-woven fabric used as starting material has a total area density of approximately 107±15 g/m<sup>2</sup>.

[0036] If the purpose is to manufacture bullet-proof garments, the starting pre-impregnated fiber sheet will preferably be impregnated only with resins. Impregnation can be carried out on one or both sides of the fiber sheet, depending on the intended result. If resin is applied on only one side of the fiber sheet, the resulting total area density of the non-woven fabric will be of about 125±15 g/m<sup>2</sup>, that is, will increase by about 17% with respect to the initial total area density. If impregnation is made on both sides of the non-woven fabric, the total area density achieved will be of about 138±15 g/m<sup>2</sup>.

[0037] If the purpose is to obtain a piercing-proof garment, it is then necessary to impregnate the fiber sheet with resins as well as the filler material. If the resin and the filler material are added on only one side of the non-woven fabric, the total area density will become of 170 g/m<sup>2</sup>, while if resin and filler are applied to both sides of the non-woven fabric, the total area density will become of 234 g/m<sup>2</sup>.

[0038] While the quantity of resin applied is the same in the different processes, the quantity of filler material added will determine the number of non-woven fabric layers necessary to form the multi-layer non-woven fabric material; the higher the quantity of filler material added, the lesser will be the number of non-woven fabric layers needed.

[0039] To obtain the multi-layer non-woven fabric material of the present invention, besides adding the resins and/or fillers to the non-woven fabrics, the non-woven fabric layers must be oriented in a specific way to obtain a performance against the penetration of bullets, cutting objects and piercing objects in compliance with standards 0101.06 and 0115.00 of the US National Institute of Justice, all in the same product.

[0040] Unexpected results have been obtained using non-woven fabrics made of aramide/polyethylene, impregnated with resins and superimposed so that the angle formed by the fibers in two adjacent non-woven fabric layers (or laminate) is different from zero degrees. Such an intercrossing of fiber orientation of adjacent non-woven fabric layers significantly reduces the size of the openings or gaps among the fibers. A smaller opening between fibers is one of the reasons behind the increased resistance of the disclosed material to piercing objects. Undoubtedly, the higher the number of non-woven fabric layers with fibers sheets at different angles, the smaller will be the openings between fibers; hence the penetration by a piercing object will be less probable.

[0041] According to the above description, resins were used to impregnate non-woven material made of aramide/polyethylene fiber sheets. The impregnation was carried out after properly placing each of the non-woven fabric sheets, one on top of the other. The incorporation of resins in the impregnation process, allowed decreasing the number of non-woven fabric layers for their testing against a cutting object. The use of a material formed by non-woven fabric layers

impregnated with resin and superimposed so that their fibers form a certain angle therebetween, allows an improvement of about 30 to 50% in comparison with a material formed by intercrossed non-impregnated non-woven fabric layers.

[0042] The assembly of flexible layers of the invention will not be attached to each other, that is, there will be no adhesive between them, thus forming a material made of multiple non-woven fabrics or multiple layers stacked or superimposed, that will become a part of a protective garment or piece of clothing. The only attachment between such pieces of non-woven fabric will be along the edges of the garment, so as to allow the non-woven fabric to adopt the intended shape of the garment. Said garment or piece of clothing made with the material of the invention, depending on the number of superimposed non-woven fabric layers and the use of resins, will withstand the penetration of cutting/piercing objects in compliance with levels 1, 2 and 3 Spike, P1 and S1 of the NH 0115.00 Standard and/or to the penetration of bullets in compliance with protection levels IIA, II and IIIA of NH 0.101.06 Standard.

#### EXAMPLES

[0043] 1) Impregnation with Resins

[0044] A roll of non-woven fiber sheet made of aramide/polyethylene fibers (GoldShield GN 2115®/2117-2118/Spectra Shield SR 1224-Spectra Shield II 3124-3130 of Honeywell) with a total area density of 107 g/m<sup>2</sup> is spread and impregnated on one of its sides with 18-25 g/m<sup>2</sup> of a polyurethane resin (Rhesinex 4) under a pressure of approximately 146 psi (10 bars) and a temperature of about 130°C. (266°F.). After impregnation with resin, a fiber sheet with a total area density of about 125 g/m<sup>2</sup> is obtained. The same process is carried out, now impregnating both sides of the fiber sheet instead of just one, thus obtaining a fiber sheet with a total area density of about 138 g/m<sup>2</sup>.

[0045] Referring now to the drawings, and more particularly FIG. 1, the present invention includes a non-woven multi-layer non-woven fabric structure 9 comprising two sets of fiber sheets or prepreg 5 of 110 grs/m<sup>2</sup> joined through gluing at angles of 0°/90° respectively and another two sets of fiber sheets 6 of 110 grs/m<sup>2</sup> joined through gluing at angles of 30°/120° respectively. This process creates two composite sheets 7 of 0°/90°, and 8 30°/120° which are overlaid as composite sheet 8 is further joined to laminates or non-woven fabric layers 7 through an angle of 30° forming a final laminate 9 forming angles of 0°/90°/30°/120°.

[0046] This process is repeated with the same fiber sheets of 110 grs/m<sup>2</sup> through various angles as shown and discussed in FIGS. 2-4. FIG. 2 shows two sets of fiber sheets 10 joined at angles of 0°/20° respectively forming a fiber layer 11 with angles of 0°/20°. This process is continued with fiber sheets 12, 14, 16, 18, and 20, forming fiber layers 13, 15, 17, 19, and 21, at angles of 0° and 25°, 30°, 35°, 40°, and 45° respectively.

[0047] FIG. 3 shows the continued overlaying of fiber sheets 22, 24, 26, 28, 30, and 32, forming fiber layers 23, 25, 27, 29, 31, and 33, at angles of 0° and 50°, 55°, 60°, 65°, 75° and 45° respectively. And finally FIG. 4 shows the last fiber layer 35 from the overlaying and joining of sheets 34 at an angle of 0° and 80°.

#### Comparative Tests

[0048] A) Ballistic test

[0049] B) Piercing and stabbing test

[0050] A) Ballistic results: This test was performed on two different materials. The first material was made by superimposing 30 non-woven fabric layers as manufactured (non traced fabrics). A second multi-layer material was made according to the present invention, and consisted of 30 non-woven fabric layers superimposed with the crossing angles mentioned above (traced fabrics).

[0051] Comparing the ballistic test results of traced fabrics (defined as those with fibers oriented at different angles) with those of non-traced fabrics (defined as those with fibers oriented at angles of 0/90°) it can be observed that the projectiles, upon penetrating the multi-layer non-woven fabric material of the present invention, exhibit a greater degree of deformation, which means that the material made with traced fabrics of the present invention dissipates energy more efficiently than the material made with non traced fabrics. Such an improvement bears a direct relationship with the ballistic performance regarding penetration of a projectile, since it is observed that the projectile penetrates a lower number of layers, thus providing greater protection and safety to the user. The traumatic effect was reduced by 25% as compared to the results obtained with the original material, with fabrics intercrossed at angles of 0°/90°.

[0052] 1) By incorporating resin on one side of the non-woven fabric, even better results are obtained regarding the deformation of incoming projectiles, number of layers penetrated, energy dissipation and displacement of threads in the area affected by the projectile. The use of these non-woven fabrics leads to a reduction of 36% in the traumatic effect as compared to standard fabrics with no intercrossing or impregnation.

[0053] 2) By incorporating resin to both sides of the non-woven fabric used for the material of the invention, the results are even better, in terms of greater protection obtained from the non-woven fabrics, greater dissipation of kinetic energy and lower traumatic effect, thus providing greater protection as compared to the material made with fabrics which have been resin-impregnated on only one side, and leading to a traumatic reduction of 50%.

#### B) Results of Piercing and stabbing Tests

[0054] 1) The original non-woven fabric as manufactured (0°/90°) is taken as a reference. Using same number of non-woven fabric layers the axial system with tracing was incorporated to the original non-woven fabric 0°/90° as produced by the manufacturer,

[0055] 2) As mentioned above, Goldshield 2112/2115/2116/2117/2118/Spectra Shield SR 1224-Spectra Shield II 3124-3130, materials are compatible with our disclosure. But only when incorporating the tracing system we were able to obtain advantageous results regarding the performance against piercing and cutting objects as compared to the non-woven fabrics used in their original condition 0°/90°.

[0056] 3) These parameters were tested and confirmed at three National Institute of Justice (NIJ) accredited HP White laboratories in the US under the NIJ-0.115.00 standard.

[0057] 4) After confirming the validity of these results in this prestigious laboratory, we continued the development of the materials of the invention by incorporating the use of resins.

[0058] 5) The incorporation of resins resulted in the obtaining of better results, in comparison to those described above. The resistance to penetration of piercing and cutting

objects was improved, and the number of necessary non-woven fabric layers was significantly reduced.

[0059] 6) By adding a filler material to the resin, even better results were obtained, since the number of non-woven fabric layers to achieve the same performance can be reduced even further. Therefore, by applying the three systems together: intercrossing of fibers, plus the use of resin, plus the incorporation of a filler material, the total number of non-woven fabric layers can be reduced by about 50%.

[0060] The foregoing discussion discloses and describes merely exemplary embodiments of the present invention. One skilled in the art will readily recognize from such discussion and from the accompanying drawings and claims, that various changes, modifications and variations can be made therein without departing from the spirit and scope of the invention as defined in the following claims.

1. A multi-layer material composed of impregnated and axially-oriented fiber fabrics comprising at least two non-woven fabric layers made of axially-oriented fibers and placed one on top of the other wherein the fibers in one of the fabric layers forming an angle different from zero degrees with respect to the fibers in the adjacent fabric layer.

2. The multilayer material of claim 1, wherein said fabric layers have been impregnated with resin.

3. The multilayer material of claim 2, wherein said fabric layers have been further impregnated with a filler material.

4. The multilayer material of claim 1, wherein the fibers of said non-woven fabric layers are aramide fibers.

5. The multilayer material of claim 1, wherein the resin is a polyurethane resin.

6. The multilayer material of claim 1, wherein the angle between the fibers in one fabric layer and the fibers in the nearest adjacent fabric layer is of 45°.

7. The multilayer material of claim 3, wherein the filler material used is SiO<sub>2</sub>.

8. A method to obtain the multi-layer material according to any of the preceding claims comprising:

impregnating a non-woven fabric comprising aramide fibers with a resin;

adding a filler material into said resin-impregnated fabric; cutting the fabric into multiple fabric pieces according to a given cutting pattern; and

superimposing multiple fabric layers to form the multi-layer material,

wherein said fibers of the fabric form angles of 0°/90°, 0°/20°, 0°/25°, 0°/30°, 0°/35°, 0°/40°, 0°/45°, 0°/50°, 0°/55°, 0°/60°, 0°/65°, 0°/70°, 0°/75°, 0°/80° with respect to the longitudinal axis of the cutting pattern; and wherein said fibers in one fabric layer form an angle of 45° with the fibers in the adjacent fabric layer.

9. The multilayer material of claim 1, wherein said material forms a protection garment.

10. The multilayer material of claim 9, wherein said protection garment is a bullet-proof vest.

11. The multilayer material of claim 3, wherein said material forms a protection garment.

12. The multilayer material of claim 11, wherein said protection garment is a multi-threat body armor.

13. The multilayer material of claim 9 or 12, wherein said impregnated and axially-oriented fiber fabric layers of said multi-layer material are only attached along the edges of the garment.

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# Carbon Nano Material Synthesis from Polyethylene by Chemical Vapour Deposition

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## ABSTRACT

Three different types of Polyethylene family, High Density Polyethylene, (HDPE), Low Density polyethylene (LDPE) and Linear Low Density polyethylene (LLDPE) polymers having different molecular weight and density; were pyrolyzed in the temperature range of 550°C - 1050°C under H<sub>2</sub>, N<sub>2</sub> and Ar gases. Taguchi Optimization technique was applied to find out the best operating conditions to get maximum yield of carbon nano material (CNM). For Taguchi optimization, experimental set up was done in two different temperature ranges i.e. 550°C - 750°C and 850°C - 1050°C. CNMs synthesized were characterized by SEM, TEM, Micro Raman and XRD analysis. HDPE was found to yield maximum CNM. Its pyrolysis at 750°C under hydrogen atmosphere for 2h gave carbon nano beads and some carbon nano tubes. Whereas under same conditions at 1050°C more multi wall carbon nano tubes (MWCNT) were produced, with some carbon nano beads. XRD data confirmed the graphitic nature of carbon-nanotube. The intensities of G-band and D-band of Raman spectra suggested that CNM has more defect sites and spectra were similar for CNM obtained in both the temperature ranges. The TGA analysis of CNM obtained at 550°C - 750°C, indicated that they are not amorphous carbon and CNM obtained at 850°C - 1050°C decomposed at 624°C - 668°C; suggesting that CNT synthesized at this temperature range were more crystalline than what was obtained at the 550°C - 750°C.

**Keywords:** Polyethylene; Pyrolysis; LDPE; HDPE; LLDPE; Carbon Nano Material (CNM); Carbon Nano Beads (CNB); Carbon Nano Tubes (CNT)

## 1. Introduction

Discovery of carbon nano material (CNM) in 1991 [1] has attracted enormous attention of scientists; because of their unique structural, chemical, mechanical and electrical properties. In order to utilize CNM for commercial applications, efforts are being made to reduce the cost of its production. Because of its simplicity, CVD technique has been found to be the most popular technique for the large scale production of CNM. One of the factors controlling the price of the CNM is the precursors used for its production. The conventionally used precursors are expensive petro-derivatives e.g. benzene, acetylene etc. However, plant derived waste products like camphor, oils of non-edible plants [2-5] have also been tried, in our lab as source of cheaper precursor.

In our pursuit of getting a cheaper precursor we have directed our efforts to use waste plastics; especially polyethenes of thickness of less than 50 µm that are creating environmental disposal problems. Since these ma-

terials are composed of polyethylene (PE) and contains long linear or branched chains of hydrocarbons (which are a good precursor for synthesis of CNM) it was thought to be appropriate to develop the pyrolysis technology to synthesize CNM from waste plastics. This attempt will not only solve the problem of disposal of waste plastic in most ecofriendly way (as it converts plastic in absence of oxygen, thus does not produce oxidized toxic carbon compounds like carbon monoxide and dioxane) but also converts the waste (plastic) to wealth (CNT). There has been efforts made in this direction, but due to proprietor and patentable nature of the work, there are very few publications available.

In order to establish conditions of synthesis of CNM from waste plastics, it was decided to develop the technique for the synthesis of CNM first from virgin PE polymers. This was necessary because the waste plastic may contain mixture of different types of polymers. In this paper results obtained with only virgin polymers are discussed; though we have successfully synthesized CNT

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using same methodology from waste PE also. Application for getting patent has been applied; hence detail cannot be disclosed at present.

Since there were more than 3 parameters involved for pyrolysis techniques and each parameter was with 3 variables, it was decided to use Taguchi Optimization Technique to find out the most suitable parameters of pyrolysis that can give maximum yield of CNM [6-8].

### 1.1. Taguchi Optimization Methodology

In a pyrolysis process the product's quality and quantity varies widely due to the parameters like temperature, flow rate and type of carrier gas, catalyst and precursor etc. Each parameters can have several levels. For example, temperature can have a range from 400°C to 900°C. Likewise other parameters will also have various levels. Considering these factors, the number of experiments becomes enormous to select the most effective parameters which can give the desired product. Taguchi Optimization Technique gives an opportunity to carry out minimum number of experiments yet giving the best desired parameters and its level to get the desired product [9,10].

Taguchi method is based on calculating the statistical analysis of "Orthogonal Arrays" (OA) of data [11,12]. The ANOVA is used to analyse the results of the OA experiment to determine how much variation in each parameters has contributed towards the production of desired product. This is found out by calculating the Signal-to-Noise ratio. Signal-to-Noise ratios (S/N) are log functions of desired output. If our interest is in getting product with largest quantity, then "larger the better" is used for such calculation. This is calculated by using the Equation (1):

$$S/N = -10 \log_{10} \left[ (1/n) \sum 1/y_i^2 \right] \quad (1)$$

where "y<sub>i</sub>" is the mean response calculated as  $y = 1/n \sum y_i$  and  $n$  is the number of experiments carried out under similar conditions.

### 1.2. Calculation for Effect of Each Parameter

To determine the effect of each parameter level ( $m_i$ ) average value of S/N ratios is calculated for each parameter using "Analysis of Mean" (ANOM) [9-13]. For this calculation the S/N ratios of each experiment with corresponding parameter levels are calculated using Equation (2).

$$m_i = (1/n) \sum S/N \quad (2)$$

Two types of average value of S/N ratio are calculated. One is overall mean S/N ratio calculated from the entire experiments viz. from nine experiments of L9 orthogonal array (**Tables 1 and 2**). The second average S/N ratio is calculated for each parameter from Equation (1).

Sum of Squares (SOS) are calculated by using Equation (3),

$$SOS = \sum n(m_i - \langle m_i \rangle)^2 \quad (3)$$

where,  $\langle m_i \rangle$  is average value of  $m_i$ .

The total Degrees of Freedom (DOF) is considered as (number of levels of parameters minus one). If there are three levels for each parameters then DOF = 2.

Factor of Effect (FOE) are calculated from Equation (4),

$$FOE = \frac{SOS}{DOF \times (SOS/DOF)} \quad (4)$$

From this FOE the percentage effect of each parameter on the production of the desired product is calculated. The main advantage of this technique is that, if for example there are 4 parameters each having 3 variables, and if they are to be repeated for 3 times, the total number of experiments becomes very large. Taguchi Optimization requires only 27 experiments if they are to be repeated three times. It is for these advantages, we have used Taguchi Optimization technique in the present work.

## 2. Material and Methods

Pyrolysis of three types of PE i.e. High Density Polyethylene, (HDPE), Low Density polyethylene (LDPE) and Linear Low Density polyethylene (LLDPE) polymers was performed. The parameters considered were 1) two different ranges of temperature i.e. lower temperature range (550°C - 750°C) and higher temperature range (850°C - 1050°C); 2) the carrier gases namely, hydrogen, nitrogen and argon and 3) duration of pyrolysis namely 1, 2 and 3 h. In order to calculate the impact of parameters on the production of CNM, factor effect was also calculated. Details of the methodology for the calculations of Taguchi Optimization technique are discussed elsewhere [6-8].

### Different Parameters & Their Levels for L-9 Orthogonal Matrix

As per Taguchi optimization methodology, two tables were constructed from the various combinations of all possible parameters with a minimum of three variables of each parameter. Variable parameters were selected which are orthogonal to each other. These parameters were: pyrolysis temperature, duration, carrier gas and type of polyethylene. Since, Taguchi Optimization technique can use only three levels of a parameter; two separate orthogonal tables were constructed, one orthogonal table utilizing 550°C - 750°C and the other table using 850°C - 1050°C temperature. Thus, two L9 orthogonal tables were constructed by using the parameters and their levels as mentioned in **Tables 1 and 2**. Nano powder of iron was used as Catalyst and it was kept same for all experiments.

**Table 1.** The orthogonal array of parameters to be optimized by Taguchi method and their impact on yield of CNM at 550°C - 750°C (Table also shows the percentage yield of carbon nanomaterial obtained and calculated values of signal to noise ratio).

Expt. No.	Pyrolysis Conditions and Yield of CNM					
	Polymer	Temperature (°C)	Gas	Duration (min)	CNM % yield	S/N
L1	LDPE	550	H <sub>2</sub>	60	0.9	-20.9
L2	LDPE	650	N <sub>2</sub>	120	0.2	-33.9
L3	LDPE	750	Ar	180	3.6	-8.8
L4	HDPE	550	N <sub>2</sub>	180	0.1	-40
L5	HDPE	650	Ar	60	14.0	2.9
L6	HDPE	750	H <sub>2</sub>	120	28.5	9.1
L7	LLDPE	550	Ar	120	0.1	-40
L8	LLDPE	650	H <sub>2</sub>	180	5.2	-5.7
L9	LLDPE	750	N <sub>2</sub>	60	3.5	-9.1

**Table 2.** The orthogonal array of parameters to be optimized by Taguchi method and their impact on yield of CNM at 850°C - 1050°C (Table also shows the percentage yield of carbon nanomaterial obtained and calculated values signal to noise ratio).

Expt. No.	Pyrolysis Conditions and Yield of CNM					
	Polymer	Temperature (°C)	Gas	Duration (min)	CNM % yield	S/N
L1	LDPE	850	H <sub>2</sub>	60	12.8	2.14
L2	LDPE	950	N <sub>2</sub>	120	6	-4.4
L3	LDPE	1050	Ar	180	0.3	-30
L4	HDPE	850	N <sub>2</sub>	180	1.5	-16
L5	HDPE	950	Ar	60	17.0	4.61
L6	HDPE	1050	H <sub>2</sub>	120	19.3	5.71
L7	LLDPE	850	Ar	120	11.5	1.21
L8	LLDPE	950	H <sub>2</sub>	180	0.8	-22
L9	LLDPE	1050	N <sub>2</sub>	60	5.6	-5

Pyrolysis was carried out for each set of condition as mentioned in **Tables 1** and **2**. Percentage yield of CNM and its S/N ratio were calculated for each experimental result by using Equation 1. The yields of CNM as well as S/N ratio calculated from each set are also given in **Tables 1** and **2**. CNM was analyzed by SEM, TEM, Micro Raman Spectroscopy, XRD and TGA.

### 3. Results and Discussions

#### 3.1. Taguchi Optimized Pyrolysis Results of Temperature Range 550°C - 750°C

**Signal/Noise (S/N) ratio** of CNM produced under different conditions is plotted in **Figure 1**. Since our interest

was to find out the condition of pyrolysis which could give the maximum amount of CNM, “Larger the Better” condition was used to calculate the S/N ratio. All those levels of parameters for which S/N ratio was more positive to the mean value of S/N ratio were considered as suitable levels for the production of CNM (**Figure 1(a)**). Amongst three types of PE polymers, HDPE appeared to give the best yield. The calculation of % impact of each parameter on the production of CNM (**Figure 1(b)**) suggests that maximum impact was that of the temperature (51.69%) followed by gas (25.12%) and then the duration (15.14%). It was interesting to note that when the pyrolysis was done in the temperature range of 850°C - 1050°C duration of pyrolysis had highest impact (84.8%) on production of carbon nano tubes (**Figure 2(b)**).

**SEM analysis**—as it can be seen in **Figure 2(a)**, at 750°C, pyrolysis under hydrogen atmosphere for 2 h duration yielded a mixture of carbon nano beads with some amount of carbon nano tubes.

**TEM micrograph**—of CNT confirmed that the CNTs are multi wall carbon nano tubes (**Figure 3**).

**XRD** peaks at 26.35 and 43.56 of carbon materials, obtained from pyrolyzing HDPE at 750°C (**Figure 4(a)**) suggests CNM to possess graphitic nature along with some amorphous carbon.

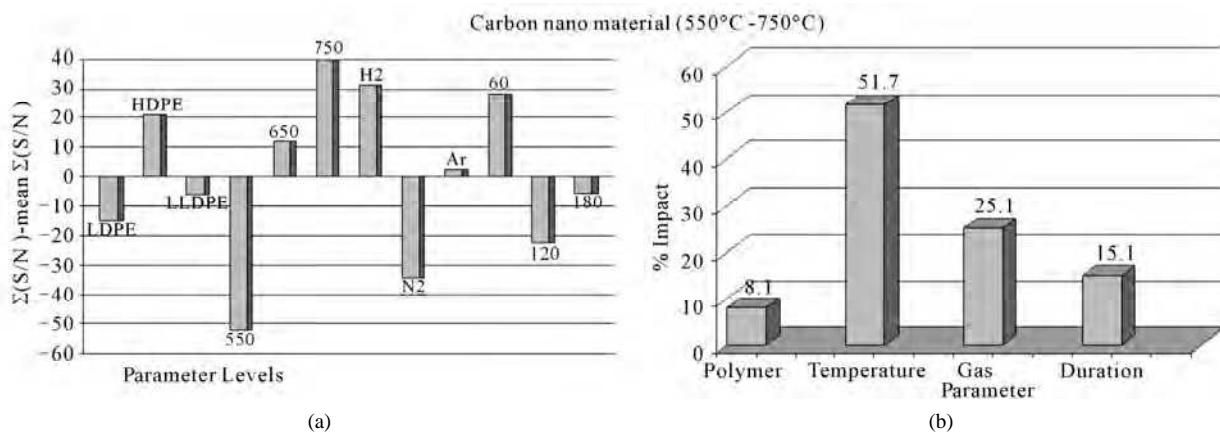
**Raman spectra** (**Figure 4(b)**) of all the samples showed almost similar results, with D-band around 1335 cm<sup>-1</sup> and G-band around 1511.11 cm<sup>-1</sup>. The intensity of G-band is less than that of D-band suggesting that CNM has more defect sites. The position of peak for G-band is more towards the D-band also supports this conclusion.

#### 3.2. Taguchi Optimized Pyrolysis Results of Temperature Range 850°C - 1050°C

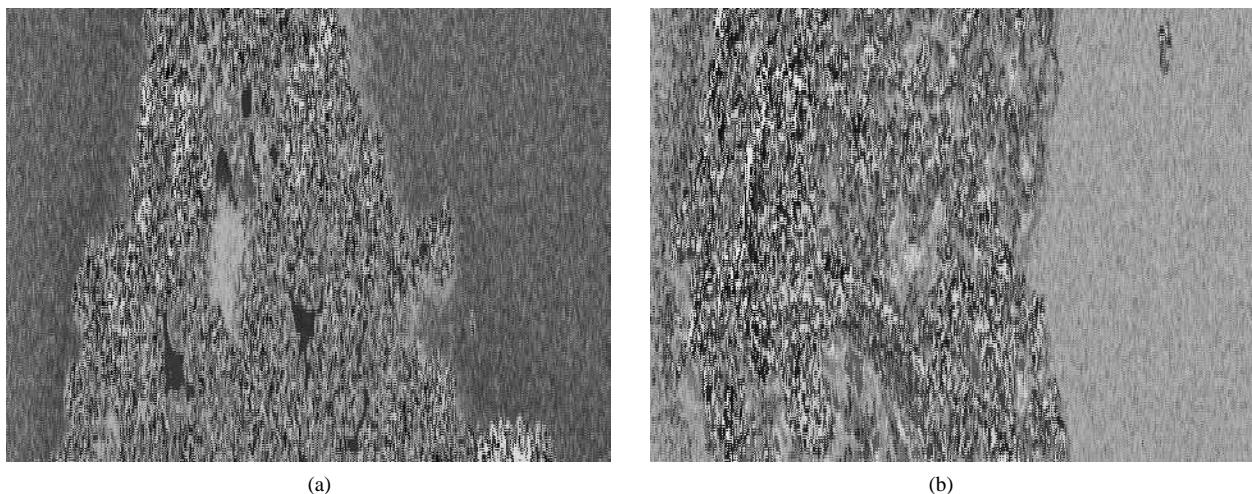
**S/N ratio**—calculation of CNM obtained by the pyrolysis of HDPE in the temperature range of 850°C - 1050°C shows that maximum yield of CNM was obtained at 1050°C in presence of hydrogen atmosphere for pyrolysis duration of 2 h (**Figure 5(a)**). It is interesting to note that while for 550°C - 750°C; temperature showed the highest % impact on the production of CNM, whereas in the range of 850°C - 1050°C, temperature had least impact i.e. only 3.5% and duration of pyrolysis had more impact of 84.78% (**Figure 5(b)**). Similar results have been observed earlier also while using plant material as precursors [8].

**XRD**—peaks (**Figure 6(a)**) of CNM obtained from pyrolyzing HDPE at 850°C, confirms the CNM to be graphitic carbon (26.3° 2θ).

**Raman spectra** were almost same for CNM produced in the temperature range of 850°C - 1050°C. Therefore, a typical Raman spectra obtained from CNT at 850°C is presented in **Figure 6(b)**, which shows D-band at 1332



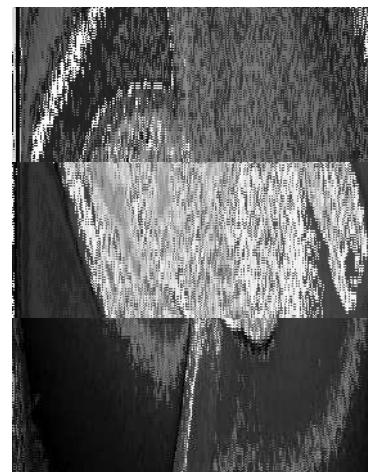
**Figure 1.** (a) Graph showing the variation in signal to noise ratio for each level of corresponding parameters. Mean value of signal to noise ratio has been taken as zero and calculation is done with “larger the better”; (b) Shows the % impact of each parameters.



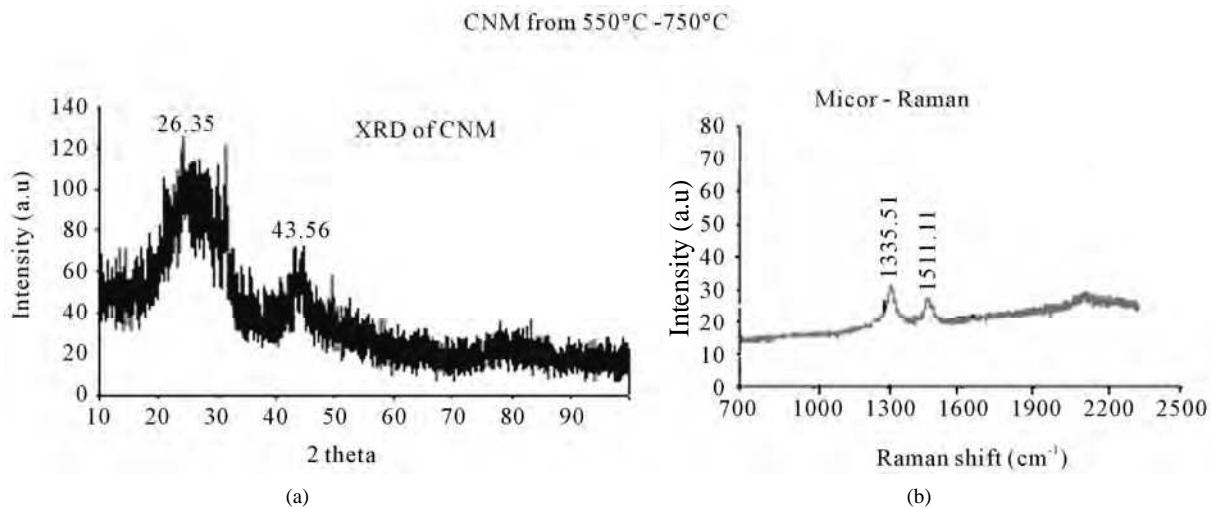
**Figure 2.** SEM micrographs of CNM obtained by pyrolyzing HDPE in hydrogen atmosphere for (a) 750°C showing mixture of carbon nano beads and some carbon nano tubes and (b) 1050°C showing more carbon nano tubes with some carbon nano beads.

$\text{cm}^{-1}$  indicating defect in graphitic carbon. Further G-band at  $1587 \text{ cm}^{-1}$  is the characteristic peak for graphitic carbon. It is interesting to note that D-band obtained with carbon produced either at 750°C or 850°C are almost the same ( $\sim 1332 - 1335 \text{ cm}^{-1}$ ), which appears at the expected peak of carbon containing defects ( $1332 \text{ cm}^{-1}$ ). However, the G-band peaks obtained with carbon produced at 750°C is at  $1511 \text{ cm}^{-1}$  while for carbon produced at 850°C is  $1587 \text{ cm}^{-1}$ . This suggests that while the defect present in both forms of these carbons are almost the same type but graphitization has taken place more at higher temperature.

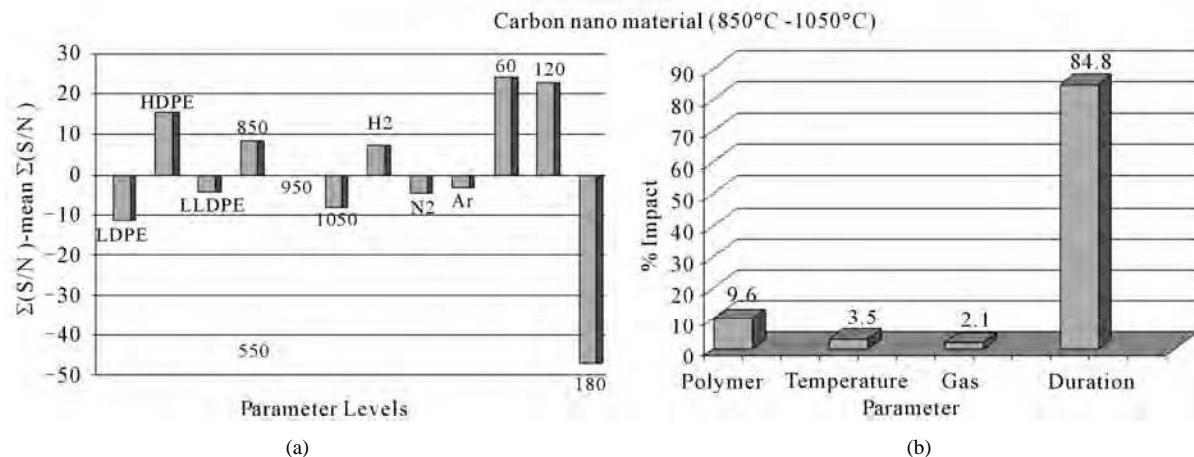
**SEM micrographs** of CNM obtained at 550°C - 750°C, and those obtained in the temperature range of 850°C - 1050°C are shown in **Tables 3** and **4** along with their TGA spectra. It is interesting to observe that CNM obtained at lower temperature range i.e. 550°C - 750°C, most of



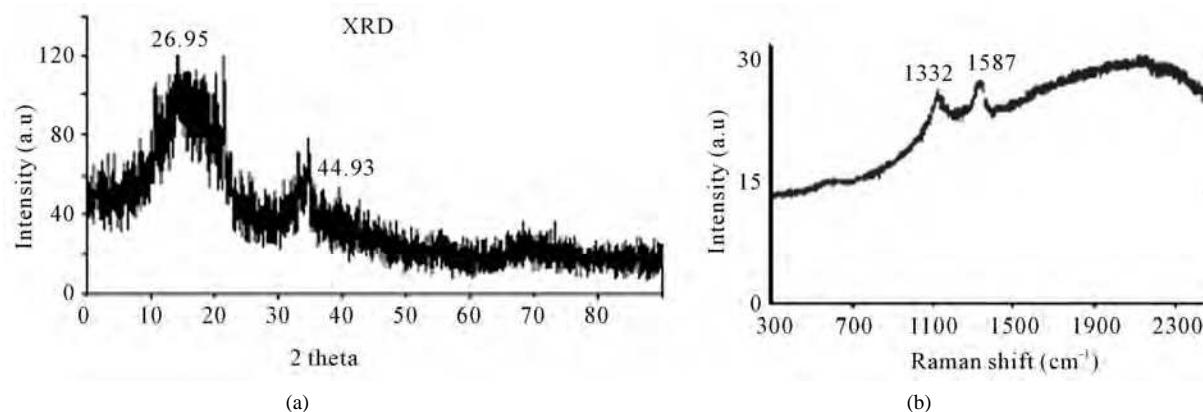
**Figure 3.** TEM micrographs of CNT (obtained by pyrolyzing HDPE in hydrogen atmosphere for 2 h at 1050°C showing coiled multi walled carbon nano tubes).



**Figure 4.** (a) XRD of the CNM produced by HDPE at 750°C shows peak at 26.35 (002) and 43.56 which are characteristic peak of the graphitic material; (b) Micro Raman spectra of CNM obtained in the temperature range 550°C -750°C.



**Figure 5.** (a) Graph showing the variation of signal to noise ratio for each level of corresponding parameters. Mean value of signal to noise ratio has been taken as zero and calculation is done with “larger the better” (850°C - 1050°C); (b) Showing the % impact of each parameters.



**Figure 6.** (a) XRD analysis of the un-purified CNM from LDPE at 850°C showing characteristic peaks of the graphitic material; (b) Micro Raman of CNM obtained from 850°C - 1050°C showing D-band at 1332  $\text{cm}^{-1}$ , indicating defect in graphitic carbon.

them are carbon beads with very small amount of carbon nanotubes. But at higher temperature beads seems to have elongated to CNTs among with some remnant carbon nano beads, hence there is a large percentage of carbon nanotubes and very few carbon nano beads. Taguchi optimization methodology has also suggested that yield of carbon nano tubes is affected more by the temperature (**Figure 1(b)**) or duration of exposure to temperature (**Figure 5(b)**) during of pyrolysis; as also noted earlier with other precursors [8]. The SEM micrographs of **Figure 2** suggest that carbon nano beads and carbon nano tubes are obtained when HDPE is pyrolyzed at 750°C and 1050°C respectively.

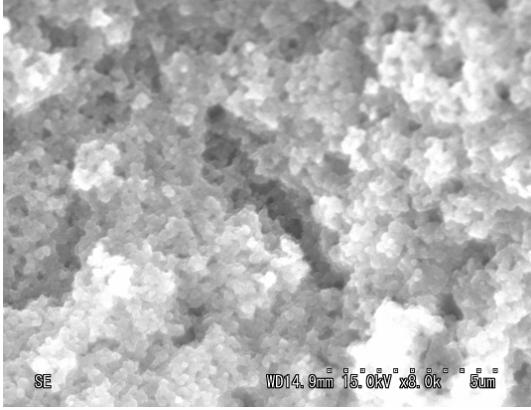
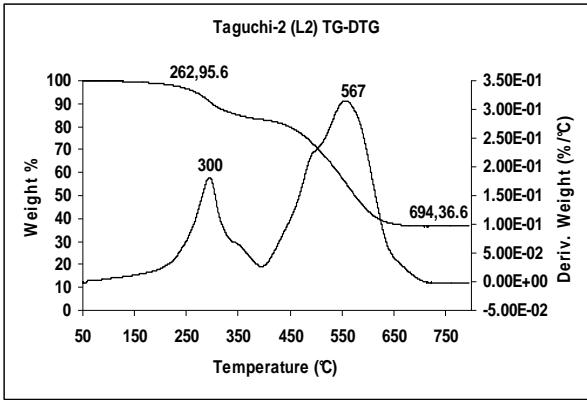
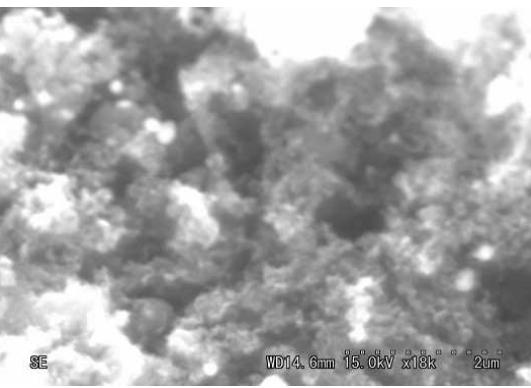
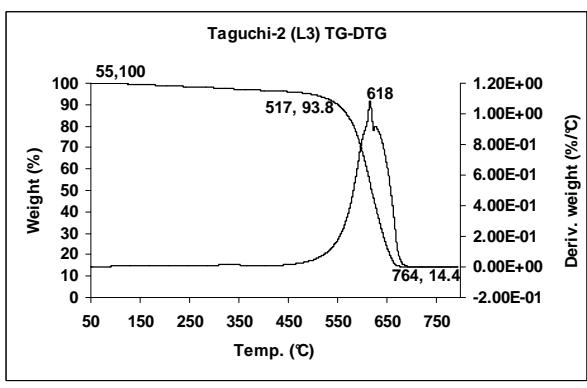
**TGA Results** of the derivatives of TGA also showed that CNM obtained at 550°C - 750°C, decomposed in the temperature range of 559°C - 648°C which is an indication that these materials are not amorphous carbon (**Table 3**). Derivatives of TGA of CNM obtained at 850°C - 1050°C shows that these materials decomposes at 624°C - 668°C; suggesting that CNT synthesized at this tem-

perature range is more crystalline than what was obtained at the 550°C - 750°C (**Tables 3 and 4**). Raman spectra also support this observation.

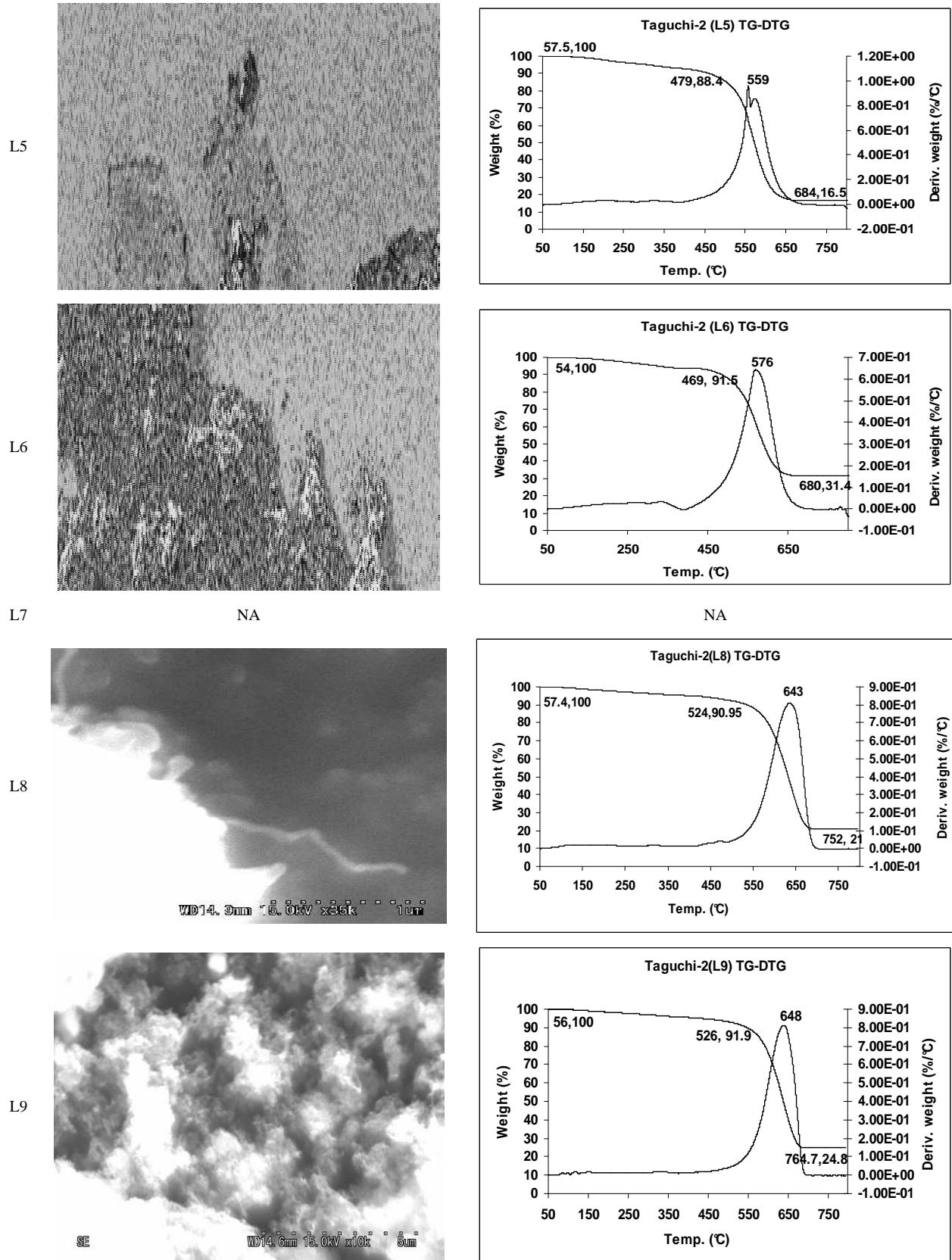
#### 4. Conclusion

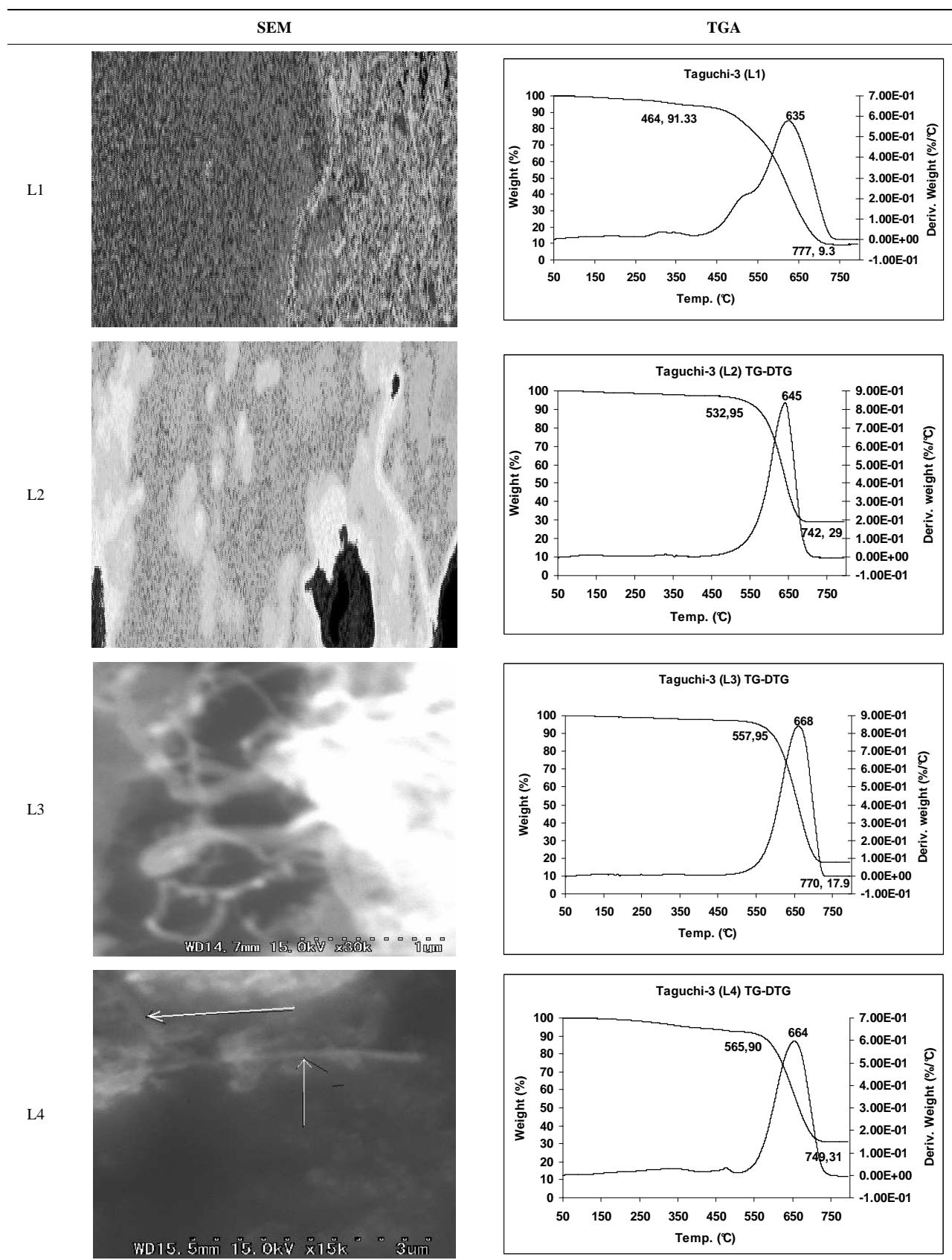
Virgin polymers (LDPE, HDPE and LLDPE) on pyrolysis using CVD system can be converted into MWCNT or CNB depending on the temperature range used. Taguchi Optimization methodology helped in selecting the best suitable parameters for high yield of desired CNM. Hydrogen atmosphere and a duration of 2 h pyrolysis was found to be the best condition for both low (550°C - 750°C) temperature range that produced CNB; as well as high (850°C - 1050°C) temperature range, which produced more MWCNT. Various characterization data viz. SEM, TEM, Micro RAMAN & TGA; all supported the same findings that CNM synthesized were graphitic, crystalline material having MWCNT or CNB morphology. Temperature higher than 600°C helped in getting rid of amorphous carbon from the CNM produced.

**Table 3. CNM Taguchi method (550°C - 750°C) analysis by SEM and TGA.**

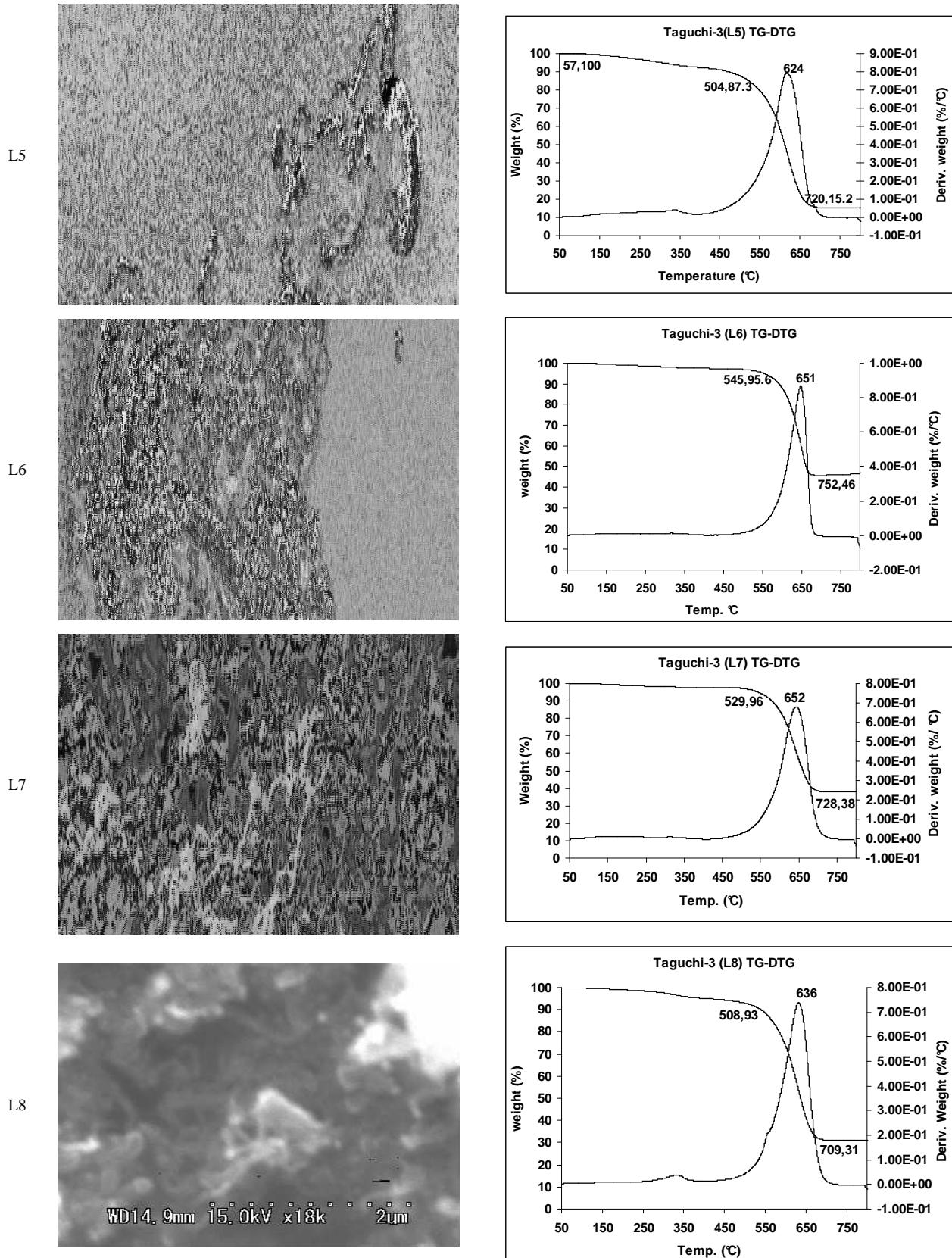
	SEM	TGA
L1	NA	NA
L2		
L3		
L4	NA	NA

Continued

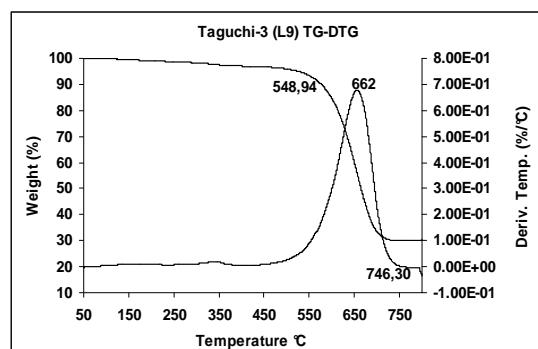
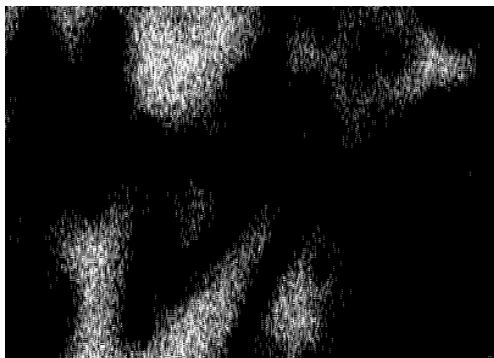


**Table 4. CNM Taguchi method (850°C - 1050°C) analysis by SEM and TGA.**

Continued



**Continued**



## 5. Acknowledgements

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## Influence of Processing Variables on the Mechanical Behavior of HDPE/clay Nanocomposites

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Nanocomposites were processed using the technique of melt intercalation, starting from a concentrated polar compatibilizer/organoclay (PE-g-MA/organoclay) prepared in an internal mixer. The concentrate was incorporated into the matrix of HDPE by two methods: I) counter-rotating twin-screw extruder and II) co-rotating twin-screw extruder, using two screw profiles (ROS and 2KB90). After extrusion, the specimens of the extruded composites were injection molded. The X-ray diffraction (XRD) technique was used to analyze the degree of expansion of the prepared clays. To analyze the degree of exfoliation of obtained nanocomposites, XRD and TEM (transmission electron microscopy) were used. The influence of processing variables on mechanical properties was studied through the behavior of the modulus and tensile strength of nanocomposite systems. By XRD and TEM, it was seen that the clay was well dispersed in the matrix and the presence of intercalated and partially exfoliated hybrid structure for nanocomposites was observed when the systems were prepared in counter-rotating twin-screw extruder. A similar behavior was observed in the use of screws (2KB90 or ROS) of the nanocomposites, with a reduction in modulus and tensile strength. Although the mixing process by extruding is the most common industrial practice, and also it is the preferred strategy for the preparation of polymer nanocomposites, much of the literature was directed to the study of chemical modification of clay, type and level of compatibilizer, in order to maximize the compatibility between clay and the polymeric matrix. On the other hand, studies about the role of the processing and configurations of screws are relatively scarce. The main motivation of this work was to expand and to contribute to spread a better understanding of the effects of processing to obtain polymer nanocomposites.

**Keywords:** nanocomposites, organoclay, mechanical behavior

### 1. Introduction

In recent years, great attention has been devoted by the polymer materials research community to the study of characteristics of the nanocomposites, especially for what concerns the understanding of the factors which leads to the desired dispersion (nanodispersion) influencing the final material properties<sup>1</sup>.

In particular, researchers have focused their attention on layered silicates (nanoclays) addressing all the possible issues related to the preparation of nanocomposites. It was proven that the addition of nanoclays to a polymer matrix brings unambiguous advantages in terms of improved mechanical properties, thermal stability, fire resistance, gas barrier, etc.<sup>2</sup>.

The smectite clays are commonly used as the dispersed phase to obtain nanocomposites, in particular, bentonite clays, for these present attractive characteristics: naturally small particles with dimensions of average size, less than 2 mm, low cost and their individual layers are reactive. Furthermore, it is possible to exchange the metal ions

by organic cations from a specific surfactant, usually a quaternary ammonium salt, turning the clay into organoclay<sup>3-5</sup>.

Polymer/clay nanocomposites are normally obtained through the dispersion of chemically modified clays (organoclays) within a polymer matrix or by in situ polymerization, merger, or solution intercalation<sup>6-8</sup>. The melt intercalation is the most promising method for large scale production.

This method consists in mixing the clay in the polymer by conventional techniques of polymer processing, in which the clay is mixed with the polymer above its softening point (for amorphous thermoplastic) or melt (for semi-crystalline thermoplastics), so this penetrates the galleries of the clay (if there is some degree of affinity between the polymer and surfactant presents in the clay) intercalating the lamella and eventually exfoliating them<sup>8</sup>.

The high density polyethylene (HDPE) is a thermoplastic resin, whose chains have few branches, so it is considered a linear polymer chain, and also for this reason, it has a high

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density compared to low density polyethylene (LDPE). It has one of the simplest structures of polymers on the market, which provides it great versatility for the variety of processes and implementation, resulting in characteristics of density, molecular weight and molecular weight distribution<sup>9,10</sup>.

Several factors affect the state of dispersion of nanocomposites: the type of organic modifier for the clay<sup>11,12</sup>, the properties of polymer matrix<sup>13</sup> and the type and concentration of compatibilizer in the system<sup>14,15</sup>. All these factors determine whether the polymer can intercalate and/or exfoliate between the layers of organoclay. But the state of exfoliation also seems to be strongly affected by processing and mixing conditions<sup>15,16</sup>. The incorporation of organoclay in the matrix is usually made in twin-screw extruders.

In this study, bentonite clay was modified by cation exchange capacity (CEC) reaction with a quaternary ammonium salt at 100% of CEC of the clay. The organoclay was mixed with compatibilizer, and the concentrate was incorporated into the HDPE matrix by two methods: I) counter-rotating twin-screw extruder and II) co-rotating twin-screw extruder, using two screw profiles (ROS and 2KB90) and injection molding. The techniques of X-ray diffraction and transmission electron microscopy were used to analyze the degree of expansion and exfoliation of developed nanocomposites. The interference of processing variables on mechanical properties was studied through the behavior of the elastic modulus and tensile strength of nanocomposite systems.

## 2. Materials and Methods

### 2.1. Materials

The materials used were: bentonite clay (1346), supplied by Bentonit União Nordeste (BUN) industry, located in the city of Campina Grande - PB. The cation exchange capacity (CEC) is approximately 90 mEq.100 g<sup>-1</sup>; Praepagen WB® (PRA - stearyl dimethyl ammonium chloride) quaternary

ammonium salt supplied in the gel state, manufactured by Clariant-PE; The used polymer matrix was high density polyethylene HDPE (JV-060U), provided by the Braskem (Camaçari/BA);

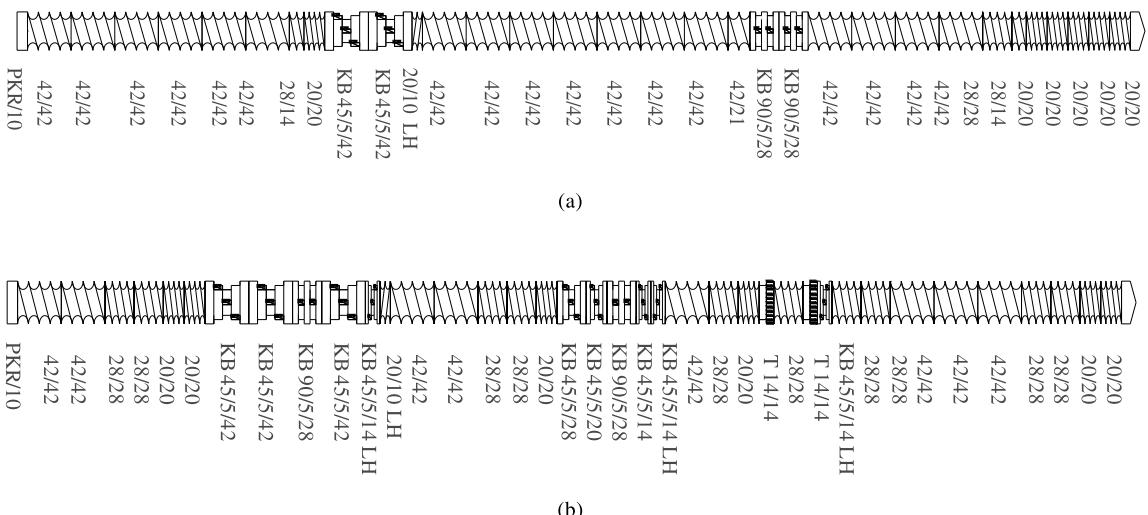
To improve the affinity between HDPE matrix and the organoclay was used polar compatibilizer Polybond 3009 (PE-g-MA), MFI = 5 g/10 min, with percentage of functionality of 1%, supplied by Crompton - Additives and olefinic Styrene - São Paulo/SP.

### 2.2. Preparation of organoclay and nanocomposites

The organophilization of clay was accomplished through the exchange of sodium ions present in the lamellar of the clay by ammonium ions to produce the organoclay at 100% cation exchange capacity (CEC) of the clay, according to studies by Araújo et al.<sup>17,18</sup>.

The preparation of systems of HDPE/organoclay/compatibilizer polar was initially performed with a master of compatibilizer/organoclay (PE-g-MA/Clay) in an internal mixer coupled with to torque rheometer of Haake Blüchler. The master was grounded, and then, it was incorporated into high density polyethylene by two methods: I) counter-rotating twin-screw extruder coupled with to torque rheometer of Haake Blüchler, II) co-rotating twin-screw extruder, with the use of two screw profiles ROS and 2KB90, (Figure 1).

The 2KB90 screw profile has been used for Polymer Processing Group at the Federal University of São Carlos-UFSCar<sup>19</sup>. It is composed of a molten barrier region at the beginning, to ensure that, from that point on, all the material is melted and is composed also by kneading blocks KB45 followed by a reverse step element. The other set of kneading blocks is composed of KB90 two elements. The profile of ROS screw has been studied for more time for obtaining nanocomposites<sup>20</sup>. The profile is composed of a molten barrier near the beginning in the screw and two sets of kneading blocks. The first is composed of elements



**Figure 1.** Screw profiles a) 2KB90 e b) ROS.

of forward and reverse pitch mixing and the second is composed of elements of the turbine to improve dispersion of the second phase and an element of reverse pitch mixture. After extrusion, the specimens of nanocomposites were molded by injection. For tensile testing, specimens were injection molded in Fluidmec model at a temperature of 200 °C at all zones, with cooling time of 25 seconds and mold temperature at 40 °C. The used concentration was at a ratio of 91:6:3 (PE: PE-g-MA: Clay).

The characterizations of the systems were made by analysis of X-ray diffraction (XRD) at room temperature by XRD-6000 Shimadzu diffractometer (40 kV, 30 mA) using CuK $\alpha$  radiation ( $\lambda = 0.154$  nm) at the rate of 2°/min in the range of 1.5–30°.

The structures were observed directly by transmission electron microscopy (TEM). TEM was carried out on a Philips CM120 with an acceleration voltage of 120 kV. Samples were cryogenically microtomed into ultrathin sections (25–50 nm thick) from Izod impact bars with a diamond knife using a RMC MT-7000 under cryogenic conditions (-80 °C) inside the microtoming chamber. A cutting speed of 0.1 mm/s was maintained throughout the microtoming operation. The ultrathin sections were collected on copper grids.

Tem mechanical characterization was used to observe the influence of modified clay and processing conditions in the properties such as, rigidity and tensile strength. Tensile tests were conducted using a LLoyd LR/10KN Universal Machine at room temperature and crosshead speed of 50 mm/min according to the standard ASTM D638<sup>21</sup>.

### 3. Results and Discussion

#### 3.1. Diffractograms of clay and nanocomposites by XRD

Figure 2 shows the organoclay XRD curves (1346-100) and systems processed by the method I (PE 3009 100) and the curve for the same composition by the method II using the two profiles screws, called 2KB90 and ROS (PE 2KB90 ORG and PE ROS ORG).

It was found that the nanocomposite system PE 3009 100 (method I) showed increased basal interplanar distance ( $d_{001}$ ) as compared to organoclay 1346-100, indicating the formation of polyethylene intercalated molecules structures between the layers of organoclay and the presence of two shoulders, probably to  $d_{002}$  and  $d_{003}$  baseline distance respectively, which may indicate that a small portion of the layers of clay was intercalated by polymer molecules<sup>22</sup>.

The co-rotating modular extruder (method II) was used to promote a better dispersion and consequently to obtain exfoliated structures. However, it is observed that these systems presented basal spacing  $d_{001}$  smaller than the organoclay and the system processed in the counter-rotating twin-screw extruder (method I), indicating that their formation was a microcomposite.

The most likely hypothesis for the basal spacing distance decrease of nanocomposites systems may have been the escape of organic cation of the clay layers during processing or break connections between the surface of the

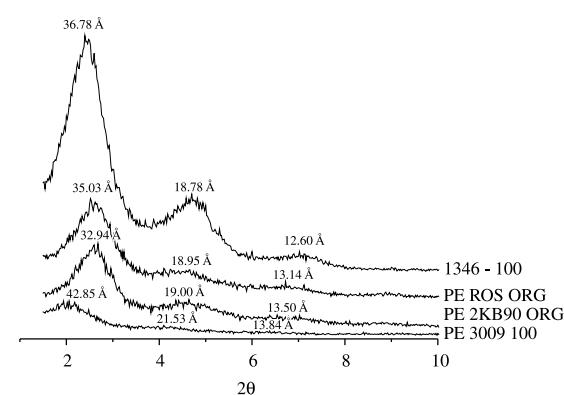
clay silicates and quaternary ammonium salt. This happened due to the effect thermal degradation during processing in the modular extruder, decreasing the basal planar distance between the clay layers<sup>23</sup>.

#### 3.2. Transmission electron microscopy (TEM).

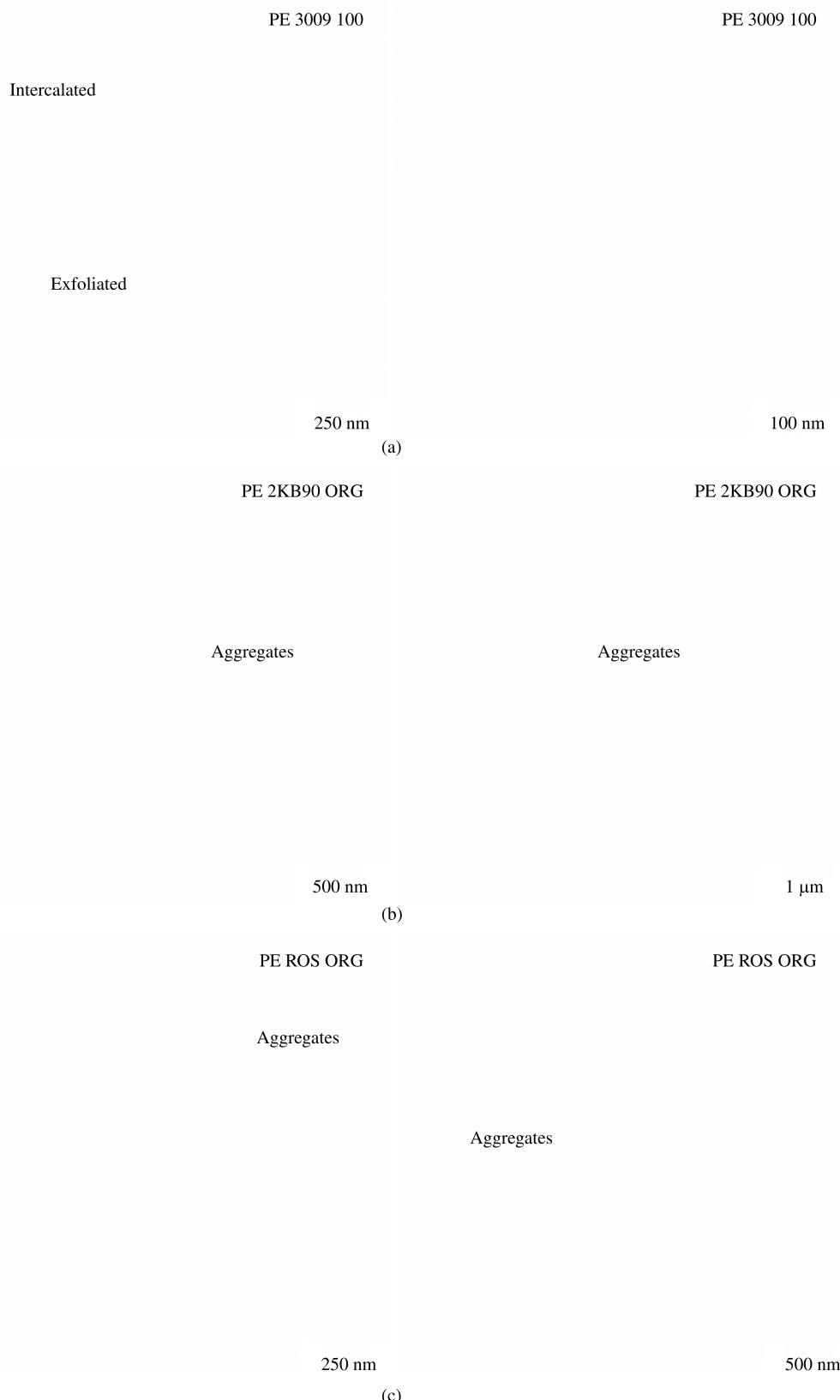
The processed systems by method I and observed by TEM demonstrate that the presence of intercalated and partially exfoliated hybrid structure can contribute to the general properties of obtained nanocomposites (Figure 3). The TEM photomicrographs of the systems processed by method II present conventional composite structures showing basically aggregates of clay. It was noticed that only the processing is not sufficient for shearing and distributing satisfactorily the load on polymer matrix even with the presence of organoclay and compatibilizers. These data corroborate with XRD results, noting that there was no affinity among the polymer matrix, clay, polar compatibilizers and processing conditions, which may be evidenced by the formation of agglomerates. The clay particles are not well dispersed in polymer matrix, probably due to poor interfacial adhesion, indicated by arrows in photomicrography. Because these screws provide the biggest effects of shearing and increased residence time during processing, it is possible that the quaternary ammonium salt, under these conditions, has migrated from the inside of the layers of clay and/or it has degraded, causing consequently the reduction of basal planar distance, and for that reason aggregates were produced.

#### 3.3. Mechanical properties of nanocomposites

Table 1 shows the values of elasticity modulus and tensile strength of high density polyethylene matrix (HDPE 2KB90 and HDPE ROS), the polyethylene/organoclay/PE-g-MA system processed by method II when 2KB90 (PE 2KB90 ORG) and ROS (PE ROS ORG) screws were used. The value of the PE 3009 100 refers to the polyethylene/organoclay/PE-g-MA system and polyethylene matrix (HDPE) obtained by method I. Figure 4 shows the stress × strain curves of the systems described above.



**Figure 2.** XRD patterns of 1346-100 clay and PE/clay/PE-g-MA systems processed in two extruders: modular co-rotating (2KB90 and ROS) and counter-rotating (PE 3009 100).



**Figure 3.** TEM photomicrographs of the systems processed in two extruders: a) counter- rotating (PE 3009 100) and modular co-rotating b) 2KB90 and c) ROS.

**Table 1.** Mechanical tensile properties of HDPE and its nanocomposites.

System	Young modulus (GPa)	Tensile strength (MPa)
HDPE	1.13 ± 0.07	22.17 ± 0.50
PE 3009 100	1.08 ± 0.04	24.00 ± 0.28
HDPE 2KB90	1.20 ± 0.08	22.92 ± 0.6
PE 2KB90 ORG	1.18 ± 0.05	22.41 ± 0.36
HDPE ROS	1.26 ± 0.11	22.87 ± 0.19
PE ROS ORG	1.21 ± 0.07	22.64 ± 0.25

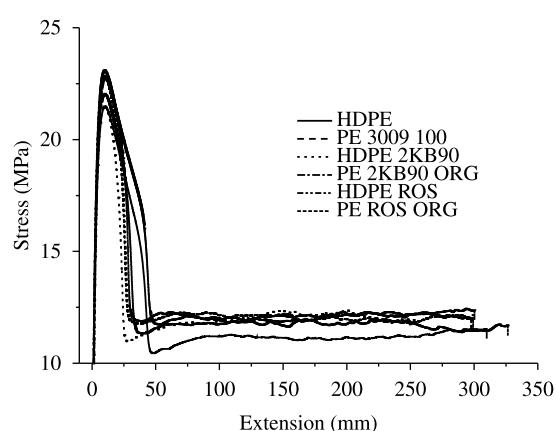
It is observed similar behavior when using the mixture screw (2KB90 or ROS). That is, the modulus and tensile strength of the systems with an organoclay (PE 2KB90 ORG or PE ROS ORG) are reduced when compared to the PE matrix (HDPE 2KB90 or HDPE ROS). Possibly, the fact that the modular co-rotating extruder (method II) was used to encourage greater dispersion, thus exfoliated structures were obtained. However, it is noticed that the processing has not been able to disperse and distribute the load in the polymer matrix successfully. Even the presence of organoclay and the compatibilizer agent was not enough to get the exfoliation, therefore reducing the mechanical properties.

#### 4. Conclusions

In this study, high density polyethylene/organoclay nanocomposites were obtained by melt intercalation technique. The nanocomposites processed in the co-rotating extruder showed basal spacing ( $d_{001}$ ) smaller than the organoclay and nanocomposites processed in the counter-rotating twin-screw extruder, and therefore a morphology of the microcomposite, as observed by TEM.

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**Figure 4.** Stress × strain curves of the nanocomposites.

In general, the presence of organoclay, compatibilizer agent and the co-rotating extruder were not sufficient to achieve exfoliation. Similar behaviors were observed when using the mixture screw (2KB90 or ROS). That is, the modulus and tensile strength of the system with an organoclay (PE 2KB90 ORG or PE ROS ORG) were reduced when compared to the PE matrix (HDPE 2KB90 or HDPE ROS).

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## Full Length Article

# Modifying friction between ultra-high molecular weight polyethylene (UHMWPE) yarns with plasma enhanced chemical vapour deposition (PCVD)

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## ABSTRACT

Ultra-high molecular weight polyethylene (UHMWPE) yarns are widely used in military applications for protection owing to its high modulus and high strength; however, the friction between UHMWPE yarns is too small, which is a weakness for ballistic applications. The purpose of current research is to increase the friction between UHMWPE yarns by plasma enhanced chemical vapour deposition (PCVD). The changes of morphology and chemical structure were characterised by SEM and FTIR individually. The coefficients of friction between yarns were tested by means of Capstan method. Results from tests showed that the yarn–yarn coefficient of static friction (CSF) has been improved from 0.12 to 0.23 and that of kinetic friction (CSF) increased from 0.11 to 0.19, as the samples exposure from 21 s to 4 min. The more inter-yarn friction can be attributed to more and more particles and more polar groups deposited on the surfaces of yarns, including carboxyl, carbonyl, hydroxyl and amine groups and compounds containing silicon. The tensile strength and modulus of yarns, which are essential to ballistic performance, keep stable and are not affected by the treatments, indicating that PCVD treatment is an effective way to improve the inter-yarn friction without mechanical property degradation.

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## 1. Introduction

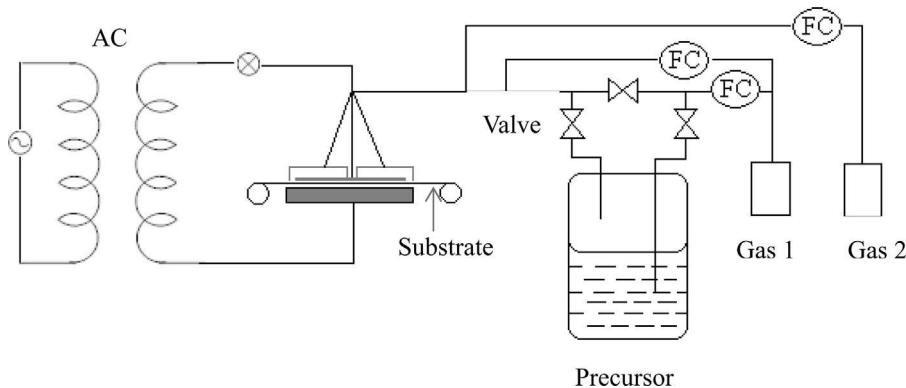
Ultra-high molecular weight polyethylene (UHMWPE) yarns, one of the commercial polyethylene-based materials and manufactured from gel-spun, is in wide use as ballistic body armour owing to its high modulus and high strength but low density, of which the tenacity is approximately ten times than steel but the density is lower than water, only 0.96 g/cm<sup>3</sup> [1,2]. Nevertheless, for ballistic protection, it's not enough just to be high modulus and strength because the inter-yarn friction also plays a significant role in preventing the yarns from being pulled out during a bullet impacting a fabric [3–6]. It has been found that higher friction between yarns at crossover provides assistance in resisting the projectile and as the inter-yarn friction approximately close to zero, energy absorption by the whole fabric panel system becomes smaller [7–10]. However, the fact is that friction between UHMWPE yarns is relatively

much smaller, compared with other fibres commonly used as ballistic materials, such as para-aramid fibre. Consequently, how to improve yarn–yarn friction for polyethylene-based materials without degrading the mechanical property provide a new challenge for body armour researchers.

Through Coulomb theory, the possibility of the friction arises from the adhesion between the surfaces, essentially from the asperities present on all surfaces. Based on this theory, several other theories of friction have been developed, but they all fall into two main divisions: the coulomb or surface roughness theory and the surface interaction theory [11]. For polymer–polymer pairs in contact, adhesion may play a dominant role and surface roughness may lead to an abrasive mechanism, if the roughness is more than nearly 0.8–1 μm [12]. Hence, modifying the surface would change the friction between yarn themselves. Nevertheless, the surface of polyethylene fibre is inert [13–15], it is impossible to modify its surface using normal chemical technology. In addition, most of the traditional chemical treatment would process at higher temperature for making the finishes more adherent to the substrate, whereas Dyneema® yarns would degrade considerable when exposure to temperature more than 160 °C.

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**Fig. 1.** Schematically illustration for PCVD under atmospheric pressure [21].

Recently, plasma treatment technology has been employed to modify the surface of fibre owing to its environment friendly and non-water effluent. Most substantial investigations showed that the surface treated by plasma become much rougher. The principle of plasma treatment is to make use of energetic particles to etch the surface of the fibre. In the etching process, some of the surfaces would be attacked and come off, causing accidented effect on the fibre and resulting in physical or chemical differences [22]. The application of plasma on UHMWPE fibre can be referred to works from Moon et al. [15–17], Lee et al. [18], Sheu and shyu [19], and Zhang et al. [20]. Although the surface of fibre treated by plasma become a little rougher but compared the surface modified by plasma enhanced chemical vapour deposition (PCVD), the increase of coarseness is far enough. This can be seen from our former research results about PCVD on para-aramid fibre [21]. Similarly to plasma treatment, the etching actions also occur during PCVD treatment, where the difference is that the plasma in PCVD can also make precursors break down to monomer polymerize or inorganic oxide deposited on the surface of fibre [23]. The precursor can be chemicals easier or not easier to react since the chemical react under higher energetic electrons or more active species created by plasma. Both the surface chemistry and surface topography are affected and the specific surface area of fibres is significantly increased by the formation of new substance on the surface of fibre. The bulk property of fibre would remain unaffected since the plasma only interacts strongly with upper molecular layers.

Accordingly, in this research, a commercial product of the UHMWPE yarns, Dyneema® yarn will be exposed to PCVD treatment for different treatment times. The differences with respect to morphology of fibre and chemical structure will be examined by SEM and FTIR respectively. The coefficients of friction between yarns as well as tensile strength after treatment will be deeply investigated as well.

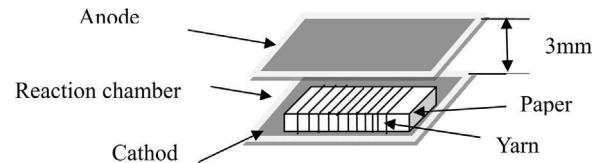
## 2. Materials and experiments

### 2.1. Materials

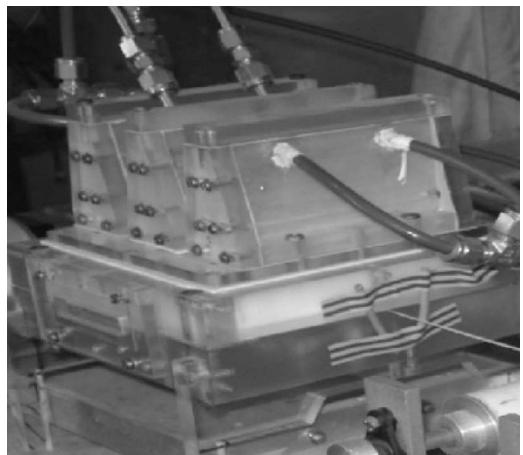
Dyneema® yarns were offered by DSM Company and the linear density of the yarn is 176 tex. The tex defined as the weight, in grams, of 1000 m of filament or yarns on the condition of commercial moisture regain. The precursor of chemical  $(\text{CH}_3)_2\text{Cl}_2\text{Si}$  is provided by University of Salford. The yarns are wrapped on a strip for the convenience of treatment.

### 2.2. PCVD treatment

The PCVD treatment is divided into two steps: the surface of the yarns is firstly activated by gas plasma followed by a second stage of



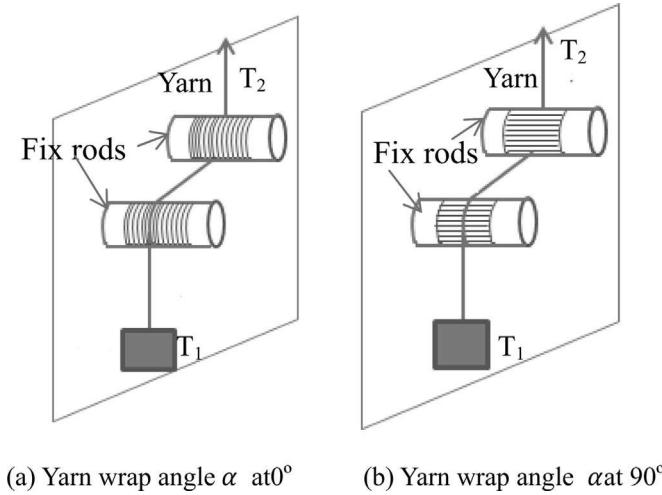
**Fig. 2.** The position of the yarn between the gap of the electrodes.



**Fig. 3.** The equipment of PCVD.

the deposition onto previously activated fibre surface. The chamber in the reactor is rectangular with size of  $10\text{cm} \times 5\text{ cm}$ . The yarns wrapped on a thin and smooth paper were positioned statically in the sample holder. The precursor of chemical  $(\text{CH}_3)_2\text{Cl}_2\text{Si}$  was thermostabilized outside the reactor and was carried in the reactor by the carrier gas.

Fig. 1 is a schematically illustration for chemical vapour deposition on yarns under atmospheric pressure which is similar to the equipment used in reference[21]but with the difference of air atmospheric pressure. The yarns were treated by means of PCVD at atmospheric pressure rather than vacuum pressure because the plasma treatment can potentially be realised with less technical effort. The position of the yarn between the gap of the electrodes is shown in Fig. 2. The gap between two electrodes is 3 mm in the reactor. Fig. 3 is the reactor for treatment. The carrier gas is nitrogen and the chemical subject to plasma action is  $(\text{CH}_3)_2\text{Cl}_2\text{Si}$ . A nitrogen plasma was chosen because of its low degrading effect and high radical density creation [17,24] and environment non-pollution. The plasma source is alternating current (AC) with input voltage 21.9 v and frequency of 3.25 kHz. The nitrogen gas flow rate is 5 l/min and the chemical flow rate is 0.2 l/min, respectively.



**Fig. 4.** Capstan method for testing coefficients of friction [25].

### 2.3. Characterization

The Fourier transform infrared spectrum (FTIR) is used to obtain the information of induced chemical changes at the micron level in treated Dyneema® yarns. The tests are conducted on equipment of NICOLET5700 FT-IR made by Thermo Electron Corporation. The spectra are recorded in the range of 4000–500 cm<sup>-1</sup> with the 32 scans and a resolution of 4 cm<sup>-1</sup> at room temperature.

The scanning electron microscope (SEM) of S-3000 was used to exam the morphology change of the yarns after treatments. Since Dyneema® fibre is an insulator, it is likely to be charging by the electron beam. An ultra-thin layer of gold is needed to coat each sample in SEM coating unit to make the fibre more electrical conductivity and signal more enhanced under the SEM observation. The specimen to be coated is positioned on a metal holder (2.5 cm in diameter).

### 2.4. Inter-yarn friction test

#### 2.4.1. Coefficient of inter-yarn friction

Coefficient of inter-yarn friction is used to indicate the friction between yarns, namely the inter-yarn friction. It is a coefficient of friction defined when one yarn is rubbed mechanically against another and capstan method is usually used to test it. Fig. 4 shows the capstan methods measured at yarn angles of 0° (a) and 90° (b) respectively. According to ASTM standard D3412-01, the coefficient of inter-yarn friction is expressed in equation 1. During the impact process, the inter-yarn friction is mainly caused by the rubbing between warp and weft yarns, which is the same as that in the case of the yarn–yarn angle of 90°. Hence, the inter-yarn friction is evaluated by the capstan method with yarn–yarn angle of 90° in present research. Consequently, the Eq. (1) to compute the coefficient of inter-yarn friction can be written as Eq. (2).

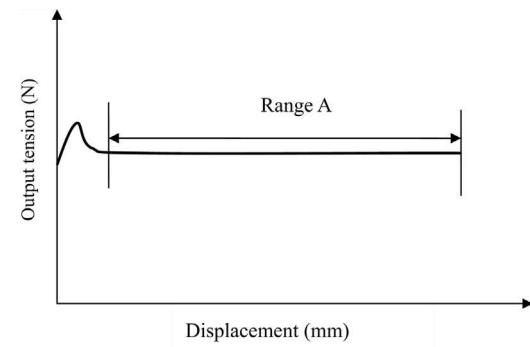
For capstan method:

$$\mu = \frac{1}{2\theta} \ln \frac{T_2}{T_1} \quad (1)$$

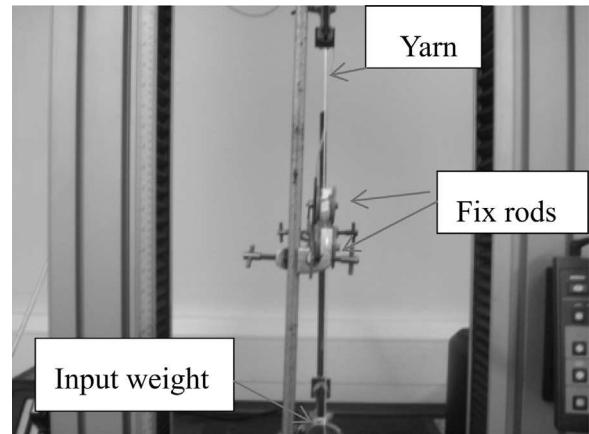
$$\mu = \frac{1}{\pi} \ln \frac{T_2}{T_1} \quad (2)$$

Where  $\mu$  means coefficient of inter-yarn friction;  $T_1$  means input tension;  $T_2$  means output tension.  $\theta$  means the yarn–yarn angle.

Fig. 5 shows a typical output tension curve observed from coefficient of friction test. The vertical axis indicates the output tension and the horizontal axis denotes the displacement. As a type of friction, the inter-yarn friction also comprises two parts, static fric-



**Fig. 5.** The typical curve from coefficient of friction test.



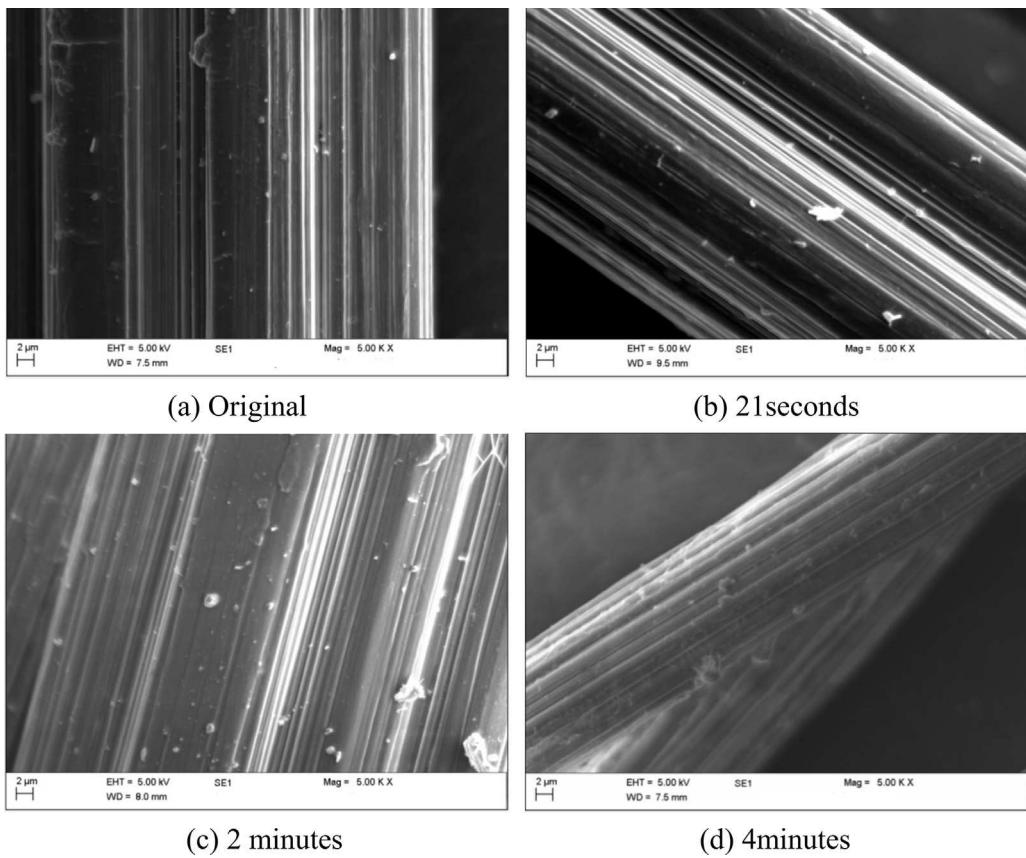
**Fig. 6.** A device used for coefficients of friction test (Instron based).

tion and kinetic friction. The largest output tension on the curve corresponds to the static friction and is used for computing the coefficient of static friction (CSF). The average output tension of range A within which the acceleration of yarn motion is 0 mm/min corresponds to the kinetic friction and is used to compute the coefficient of kinetic friction (CKF). The input tension was adjusted to provide an input tension of  $10.0 \pm 0.5$  mN/tex according to the standard. In this way, the input weight used was set to be 171.89 g for Dyneema® yarn.

#### 2.4.2. Inter-yarn friction test device

Based on the above test principle, the coefficient of inter-yarn friction tests were carried out using a device on an Instron tensile tester as shown in Fig. 6, which is the front view. The side view of the device is not shown here because of the block of arms on two sides in Instron tensile tester but it can be referred to Fig. 4(b). In the setup, two rods with diameters of 13 mm are fixed horizontally on a frame, and they are mounted on the tensile machine. In the frame, the yarn wraps the rods in the axial direction.

The displacement of the cross head is limited to 20 mm. All the tests were carried out on Instron 5500 at room temperature of 23 °C and humidity of 50%. The test speed has effects on the coefficients of friction between yarns [26]. In the ballistic impact, the speed of the yarn motion is around 10<sup>6</sup> mm/min [27]. It is impossible to test the coefficients of friction at such high loading speed because of the limitation of equipment. Thus, it is essential to build the relationship between inter-yarn friction in quasi-static state and the ballistic performance. Coefficient of friction in quasi-static state was found relatively stable when the test speed is between 0.1 yard/min to 1 yard/min [26], approximately 90 mm/min to 900 mm/min and so that the crosshead speed (the moving speed of the crosshead)



**Fig. 7.** The morphology of Dyneema® fibre treated by PCVD treatments.

was set as the intermedia value of 500 mm/min. The coefficients of friction are averaged from five samples.

## 2.5. Tensile test

The tensile strength is obtained from the machine of Instron-44. The yarn tenacity is equals to the tensile strength of one yarn divided by the yarn tex. The special gauge length is 250 mm but the total specimen is 700 mm long since the sample has to be wrapped two laps on the two clamps individually to make sure little slide happen during stretching process. In order to make the filament straight and parallel, the pretension of 0.5 cN is employed. The yarn is stretched at a speed of 250 mm/min. The temperature was set as 20 °C and the humidity as 60%. The tensile properties were the average results of eight specimen.

## 3. Results and discussion

### 3.1. SEM analysis

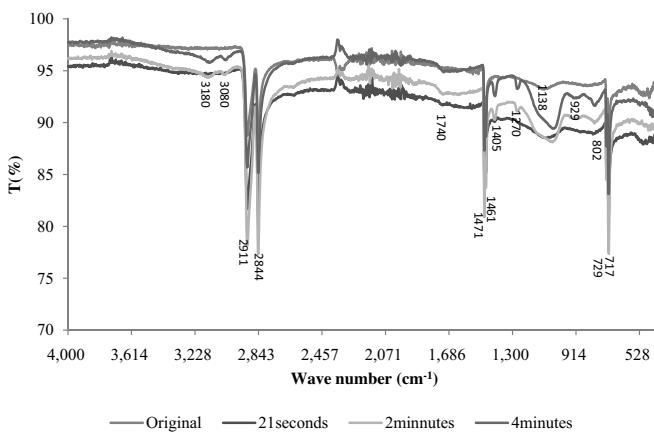
Fig. 7 characterises the morphology of Dyneema® yarns before and after treatments. Based on Fig. 7(a), it reveals that the surface of the original Dyneema® fibre is not as smooth as other synthetic fibres. The shape of the ridges and bulges on the fibre surfaces are clearly distinguished and the fibrillary nature of UHMWPE fibres is discernible. The visible lines running parallel to the fibre axis are highly defined on the original fibre surface [28]. In addition, a few impurities are scattered on the surface of the fibre. With 21-s treatment, the surface of the filament is observed not to be significantly affected. When the treatment time prolongs to 2 min, even to 4 min, the surface of the fibre is still covered with limited substance. The striation nature of the surface is not subjected to seriously damage

even when the treatment time prolongs to 4 min. It is reported that the plasma would etch the surface of the fibre because of highly energetic particles in the plasma system [29,30]. The less damage for the Dyneema® fibre may be attributed to its inherently much more inert property compared to Twaron® fibre [31]. Consequently, the same treatment conditions as Twaron® fibre are not enough to give rise to same etch effect to the Dyneema® fibre. Overall, as the time increases to 4 min, the surface of the Dyneema® fibre would be deposited with limited granular-like substances by PCVD treatment.

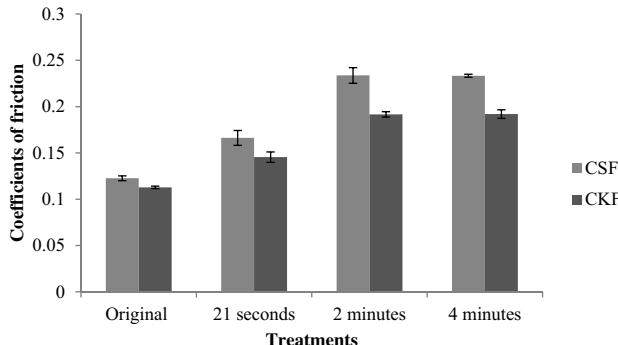
### 3.2. FTIR analysis

The FTIR spectra for original Dyneema® yarns and the ones treated for different times are shown in Fig. 8. For the original Dyneema® yarn, the strong absorptions at  $2911\text{ cm}^{-1}$  and  $2844\text{ cm}^{-1}$  are ascribed to C—H asymmetric and C—H symmetric vibrations in  $-\text{CH}_2-$ , respectively. The troughs at wave length of  $1461\text{ cm}^{-1}$  and  $1471\text{ cm}^{-1}$  are assigned to methylene and methyl bending vibration, respectively. The wave numbers at  $729\text{ cm}^{-1}$  and  $717\text{ cm}^{-1}$  are ascribed to C—H rocking vibration in structure  $-(\text{CH}_2)_n-$  [32]. The weak absorption at  $1138\text{ cm}^{-1}$  corresponds to the C—O absorption due to the impurities [33]. These absorption assignments are shown in Table 1.

A weak absorption peak at  $1740\text{ cm}^{-1}$  is discernible in the FTIR spectrum of the yarn treated for 21 s compared to the original yarn, indicating a creation of carbonyl group possible due to oxidation, mainly in forms of carboxyl groups. Also, the faintly visible broad absorption range from  $3600\text{ cm}^{-1}$  to  $3100\text{ cm}^{-1}$  is the typical absorption of hydroxyl. In addition, the absorption at wave number of  $1138\text{ cm}^{-1}$  shifts to the low wave number because of the formation of Si—O bond generated through the action between free



**Fig. 8.** The FTIR spectra of Dyneema® yarns by PCVD treatments.



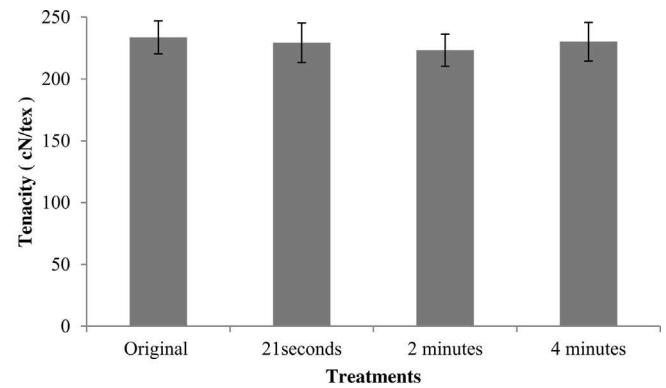
**Fig. 9.** Coefficients of friction of Dyneema® yarns by PCVD treatments.

**Table 1**  
Assignments for absorbance bands of original Dyneema® yarn.

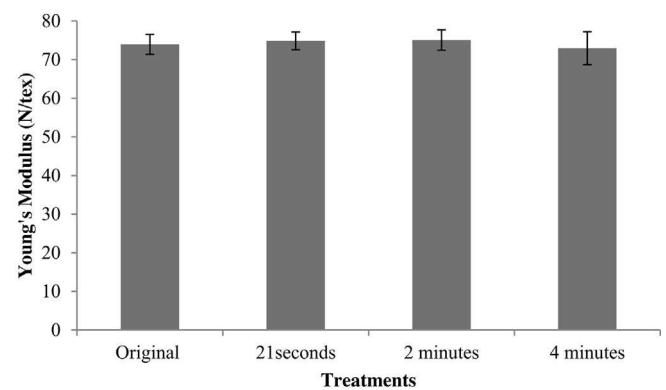
Peak(cm⁻¹)	Assignments
3153,3052	O—H stretching vibration
2911	C—H asymmetric vibration in —CH <sub>2</sub> —
2844	C—H symmetric vibrations in —CH <sub>2</sub> —
1461, 1471	methylene bending vibration
729, 717	C—H rocking vibration in structure —(CH <sub>2</sub> ) <sub>n</sub> —

radicals of silicon and the oxygen in the system. Although the surface morphology of the yarn for 21-s treatment shows little change from the SEM observation, there are still some chemical reactions taking place during the period. The free radicals in the plasma produced at or near the yarn surface can interact to form the cross-links and unsaturated groups with the chain scission. At the same time, some of the groups on the surface of the yarn would be oxidised by highly energetic particles. These two possible reactions are corresponding to the new absorption peaks on the spectra of the yarns treated for 21 s.

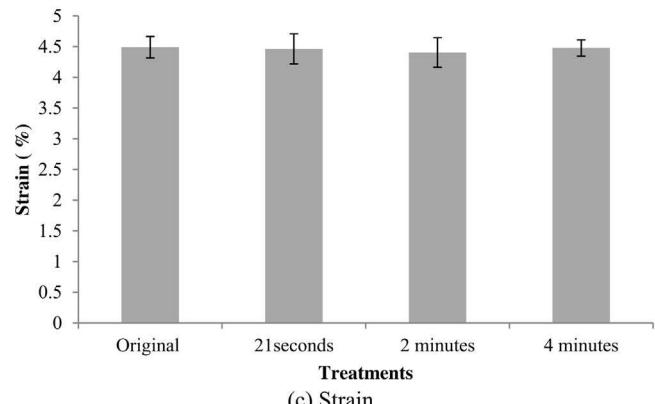
When the treatment time becomes longer, to 2 min and 4 min, the absorption at wave number 1138 cm<sup>-1</sup> shifts to 1090 cm<sup>-1</sup> due to the strong Si—O—Si stretching absorption [34] and this absorption peak becomes stronger because of more silicon oxidation are formed on the surface of the fibre. The absorption peak at frequency of 1740 cm<sup>-1</sup> and the wide band ranging from 3100 cm<sup>-1</sup> to 3500 cm<sup>-1</sup> for the hydroxyl are more noticeable. Except the absorption at the above wave numbers, FTIR results of the fibres treated for 2 min and 4 min show other new weak discernible absorptions. 3080 cm<sup>-1</sup> and 3180 cm<sup>-1</sup> may be caused by the amine group. 1405 cm<sup>-1</sup> and 1270 cm<sup>-1</sup> may be assigned to the asymmetric and symmetric vibration of methylene directly link with silicon [35]. The weak absorptions at 802 cm<sup>-1</sup> and 929 cm<sup>-1</sup> might be



(a) Tenacity



(b) Modulus



**Fig. 10.** The tensile properties of Dyneema® yarns by PCVD treatments: (a) tenacity; (b) Modulus; (c) Strain.

ascribed to Si—O bending vibration and Si—OH stretching vibration [36]. In general, some polar groups appear on the surface of the yarn, including carboxyl, carbonyl, hydroxyl and amine groups and compounds containing silicon.

### 3.3. Coefficients of friction

Fig. 9 displays the coefficients of friction of original and treated Dyneema® yarns. Based on the tests, the coefficients of friction of the original Dyneema® yarn are 0.12 for CSF and 0.11 for CKF. The obtained coefficients of friction are in agreement with the measurement in Chen et al. [37]. The coefficients of friction are also sensitive to the applied PCVD treatments. Just after 21 s, the CSF and CKF go up to 0.17 and 0.15 respectively. When the treatment time increases to 2 min, CSF and CKF can be increased by 90.61%

**Table 2**

Changes of tensile properties of Dyneema® yarns by PCVD treatments.

Treatments	Increase of tenacity (%)	Increase of modulus (%)	Increase of strain(%)
21 seconds	-1.85	-0.62	1.21
2 minutes	-4.42	-1.91	1.53
4 minutes	-1.49	-0.31	-1.34

and 69.90% respectively. However, to the yarn treated for 4 min, the coefficients of friction almost keep at that level.

It is believed that there are two components of friction, deformation and adhesion [38,39]. Increasing either components will increase the final friction. Based on SEM observations, the surface roughness of all the treated Dyneema® yarns has not been significantly affected, so the components from deformation because of asperities are not significantly affected. Therefore, the increase in inter-yarn friction after PCVD treatments may be attributed to the increased adhesion resulted from more interaction between polar groups on the treated yarn surface. For the original Dyneema® yarn, the surface of the yarn is solely covered with non-polar C–H group. The surfaces of two original Dyneema® yarns are repulsive because of the same electrical charge carried by the hydrogen atom. After treatments, the FTIR spectra confirmed that the surfaces of the yarns have been introduced a certain amount of polar groups, including hydroxyl bond, carbonyl and carboxyl groups. Hydrogen bond can develop at very short distance in polymers with the groups of –OH, –COOH, –NHCO– and others, in which the hydrogen atom is linked with an electronegative atom. Under favourable conditions, two approaching atoms are linked together by a common proton providing a strong and stable compound [38]. Based on this theory, more hydrogen bonds may be produced when the two surfaces of the treated Dyneema® yarns come into contact, which can give rise to more junctions and interfacial bonds in turn. Formation and rupture of the junctions controls the adhesion component of friction [39]. Therefore, the treated Dyneema® yarns would have larger inter-yarn friction. When the treatment prolongs to 4 min, the polar groups are not significantly increased as evidenced by FTIR analysis. Thus, the inter-yarn friction from 4-min treatment equals that from 2-min treatment.

#### 3.4. Tensile properties

The averaged values of the tensile properties of Dyneema® yarns are shown in Fig. 10. Table 2 lists the change percentages of the tensile properties after treatments. Normally, the changes of the yarn weight after treatments should be taken into account. However, as mentioned in the section of Twaron® tensile properties [31], the difficulty of measuring the changes of the yarn weights also exists in the case of Dyneema® yarns. Moreover, based on the SEM observations, the surfaces of the treated yarns are deposited with limited substances, even if the time prolongs to 4 min. Consequently, it is reasonable to study tensile properties assuming that the weights of the treated Dyneema® yarns have not been affected.

Using significance test in statistical analyses at 95% confidence interval, all P-values in each treatment condition are larger than 0.05, indicating no significant difference between the tensile properties of yarns before and after treatments. These results demonstrate that the PCVD treatment just acts on the outermost layer of the fibre, and the bulk property of the yarn remains unaffected.

#### 4. Conclusions

One of the UHMWPE yarns, Dyneema® yarns are treated by PCVD method with  $(\text{CH}_3)_2\text{Cl}_2\text{Si}$  at atmospheric pressure. With

treatment time increase, there are more and more particles on the surface of the fibre and the striation structures subject some destroy and some polar groups appear on the surface of the yarn, including carboxyl, carbonyl, hydroxyl and amine groups and compounds containing silicon. Compared with the original yarns, the yarn–yarn coefficient of static friction has been improved from 0.13 to 0.23 and that of kinetic friction increased from 0.11 to 0.19, as the samples exposure to the time from 21 s and 4 min.

It is demonstrated that the PCVD is an effective method to modify the surface morphology of Dyneema® fibre on the premise of keeping the mechanical property not affected. Since there is no research endeavouring to increase the inter-yarn friction by experiment, this research maybe shed a light on how to improve the inter-yarn friction for ballistic application. However, it should be noted that for ballistic research, the inter-yarn friction should be much larger. As such, further improving the friction between yarns is needed to explore.

#### Acknowledgements

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# Synthesis of Additives from Montmorillonite to Modify High Density Polyethylene Final Properties

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**Summary:** This work brings about the modification of sodium montmorillonite clay (MNa) by the cationic exchange with hexadecyltrimethylammonium to turn it into organophilic clay (MC<sub>16</sub>). Subsequently, MC<sub>16</sub> was treated with silanes. Three silanes with functional groups of different chemical nature were used. The objective was to determine if the clay could affect high density polyethylene (HDPE) final behavior after being modified with each silane. The following silanes were used: Cl<sub>2</sub>Si(CH<sub>3</sub>)<sub>2</sub>, Cl<sub>2</sub>Si(CH<sub>3</sub>)(C<sub>6</sub>H<sub>5</sub>) and Cl<sub>2</sub>Si(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>. Finally, in situ hydrolysis was carried out to generate the respective siloxanes. These materials were characterized by XRD, FTIR and GPC analyses. Each one of these additives was mixed using melt compounding processing in a Haake torque rheometer Rheocord 9000 equipped with a mix chamber and roller rotors at 100 rpm and 190 °C. All hybrids were characterized by XRD, SEM and thermogravimetric analyses. Barrier properties to cyclohexane were also determined by pervaporation experiments. Results from all studies showed that the addition of approximately 3 wt% of clay has changed the macroscopic properties of the above-mentioned composites, as compared with pure HDPE. This can be explained considering the different polymer/filler interactions which take place in each system.

**Keywords:** clay; compatibilization; HDPE; organic polymer/inorganic filler hybrids; siloxane

## Introduction

Thermoplastics comprise a group of polymers that offers many advantages and which has throughout time replaced other materials in more than a few applications.<sup>[1–3]</sup> These polymers are liable to changes that allow improving their performance. Nowadays, environment-friendly ways of material modification are pursued, e.g. by adding inorganic natural fillers.<sup>[4]</sup>

Polymers modified by the addition of inorganic species have been intensely studied, especially over the last years thanks to the development of polymer nanocomposites that in general show enhanced properties.<sup>[5–7]</sup>

Nevertheless, filler addition does not generally affect just one polymer property

but leads to awkward situations.<sup>[7]</sup> Some of them are: resistance to apolar solvents, mechanical properties, polymer thermal resistance, processability, etc.<sup>[8,9]</sup>

In this article, sodium montmorillonite clay (MNa) was used as precursor of high density polyethylene (HDPE) additives. This clay was superficially modified and later added to the polymer in order to analyze the effects of each treatment on final organic polymer/inorganic filler hybrid behaviors. In particular, two properties were evaluated: thermal stability and transport properties. As filler addition can influence polymer response to apolar solvents, changing barrier properties of materials, hybrids were evaluated by cyclohexane pervaporation.

Polymer thermal stability is important for the processing stage and for determining the material properties for further applications. Onset temperature provides valuable information to determine manufacturer and processability temperatures

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without starting material degradation process.<sup>[1,10]</sup>

It should be noted that superficial modifications in MNa were carried out aiming to improve the chemical affinity to HDPE.

A wide range of options can be explored seeking polymer/filler compatibility. In the case of mineral clays used as polyolefins modifiers, the selection of an appropriate compatibilizer is of crucial importance since laminar silicates can be partially or totally delaminated in order to obtain polymer nanocomposites.<sup>[11–13]</sup> In particular, compatibilization treatments have been suggested for polyethylene (PE) or polypropylene (PP), but always by using copolymers with the main chain of the same nature of the matrix and with side groups similar to clay (PE or PP grafted with maleic anhydride).<sup>[14,15]</sup> However, in this work, enhanced compatibility is proposed by using siloxanes as superficial modifiers of clays, which are afterwards mixed with the melted polymer. In this case, the modifier has the main chain of the same chemical nature of clay and of organic side groups which are compatible with HDPE hydrocarbon macromolecules.

## Experimental Part

An Argentinean MNa clay kindly supplied by MINARMCO (cation exchange capacity = 70 mEq/100 g and particle size less than 325 Mesh) was used in this work. The chemical composition of this MNa is given in Table 1.

The MNa clay was modified with hexadecyl trimethylammonium chloride (HDTMA) provided by PharmaSpecial (GENAMIN CTAC). Dimethyldichlorosilane (DMS), methylphenyldichlorosilane (MPhS) and diphenyldichlorosilane (DPhS) were purchased from Sigma Aldrich.

## Preparation of Organophilic Clay

A 5% g/mL distilled water dispersion of untreated MNa clay was prepared and quaternary ammonium salt HDTMA solution was added to the dispersion. The mixture was stirred for 2 h at 80 °C and filtered. Several washes were carried out for ensuring complete elimination of chloride ion. After negative test of the filtrate with 0.1N AgNO<sub>3</sub> solution, the organophilic montmorillonite clay (MC<sub>16</sub>) was dried at 80 °C for 48 h.<sup>[17]</sup>

## Preparation of Siloxane Modified Organoclays

Three mixtures were prepared by putting in direct contact 10 g of silane with 10 g of MC<sub>16</sub> at room temperature and they were maintained in contact for 5 days. Then distilled water was added on a H<sub>2</sub>O/Si = 20 molar ratio. After 5 days, treated clays were washed until complete elimination of Cl<sup>-</sup> ion. According to the silane used, e.g., DMS, MPhS and DPhS, the following materials were prepared: MC<sub>16</sub>-PDMS, MC<sub>16</sub>-PMPHS and MC<sub>16</sub>-PDPhS, respectively.

## Preparation of Polymeric Hybrids

HDPE/clay mixing was performed using melt compounding processing in a Haake torque rheometer Rheocord 9000 equipped with a mix chamber and roller rotors at 100 rpm and 190 °C during 10 min. The following hybrids were obtained: HDPE/MNa, HDPE/MC<sub>16</sub>, HDPE/MC<sub>16</sub>\_PDMS, HDPE/MC<sub>16</sub>\_PMPHS and HDPE/MC<sub>16</sub>\_PDPhS. All these compounds contained 97 wt% of HDPE pellets and ~3 wt% of clay.

## Characterization

X-ray diffraction analyses were performed in a Rigaku Miniflex DRX 6000 diffractometer using nickel filtered CuK $\alpha$  radiation

**Table 1.**  
Percentual composition of natural clay.<sup>[16]</sup>

Component	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	Na <sub>2</sub> O	CaO	K <sub>2</sub> O	Fe <sub>2</sub> O <sub>3</sub>	Others
wt%	62.0	18.0	3.0	3.5	2.0	1.0	7.0	3.5

operating at 30 kV and 15 mA. The data were recorded at 20° rate of 2° per minute.

The treated clays were evaluated by infrared spectra recorded in a FTIR 1720x-Perkin Elmer spectrometer using pressed KBr disks at 20 scans and 2 cm<sup>-1</sup> resolution.

Siloxanes oligomers from modified clays were obtained via soxhlet extraction with cyclohexane. The cleaned clays were dried until complete solvent elimination.

Molecular weights and polydispersity indexes were obtained using gel permeation chromatography (GPC) in an Agilent system equipped with differential refractive index detector and a linear Phenogel column. Monodisperse polystyrenes were used as calibration standards and chloroform (1 mL/min) as eluent.

Thermogravimetric characterization (TG/DTG) was performed from 25 to 700 °C at a heating rate of 10 K/min, under a N<sub>2</sub> flow (balance purge flow = 40 mL/min and sample purge flow = 60 mL/min), with a thermal analyzer TA Instruments (USA), TGA Q500.

Transport properties were evaluated using standard pervaporation equipment with cyclohexane as solvent. Film behaviors were observed at three temperatures. Vacuum was maintained using liquid N<sub>2</sub>.

Scanning electron microscopy (SEM) was carried out in a JEOL JSM-6480 LV. Samples were coated with gold in order to study the surface morphology.

## Results and Discussion

### XRD Analyses

Figure 1 shows X-ray diffractograms of unmodified and modified clays before and after melt compounding with HDPE. Comparing only clay XRD patterns, it was observed that cation exchange leads to an increase in basal distance (Figure 1b), generating at the same time a lipophilic medium between clay sheets. When silanes were added to MC<sub>16</sub> a diffusion phenomenon took place. However, after hydrolysis, only clays that were treated using MPhS (Figure 1d) and DPhS

(Figure 1e) showed higher intercalation degrees.

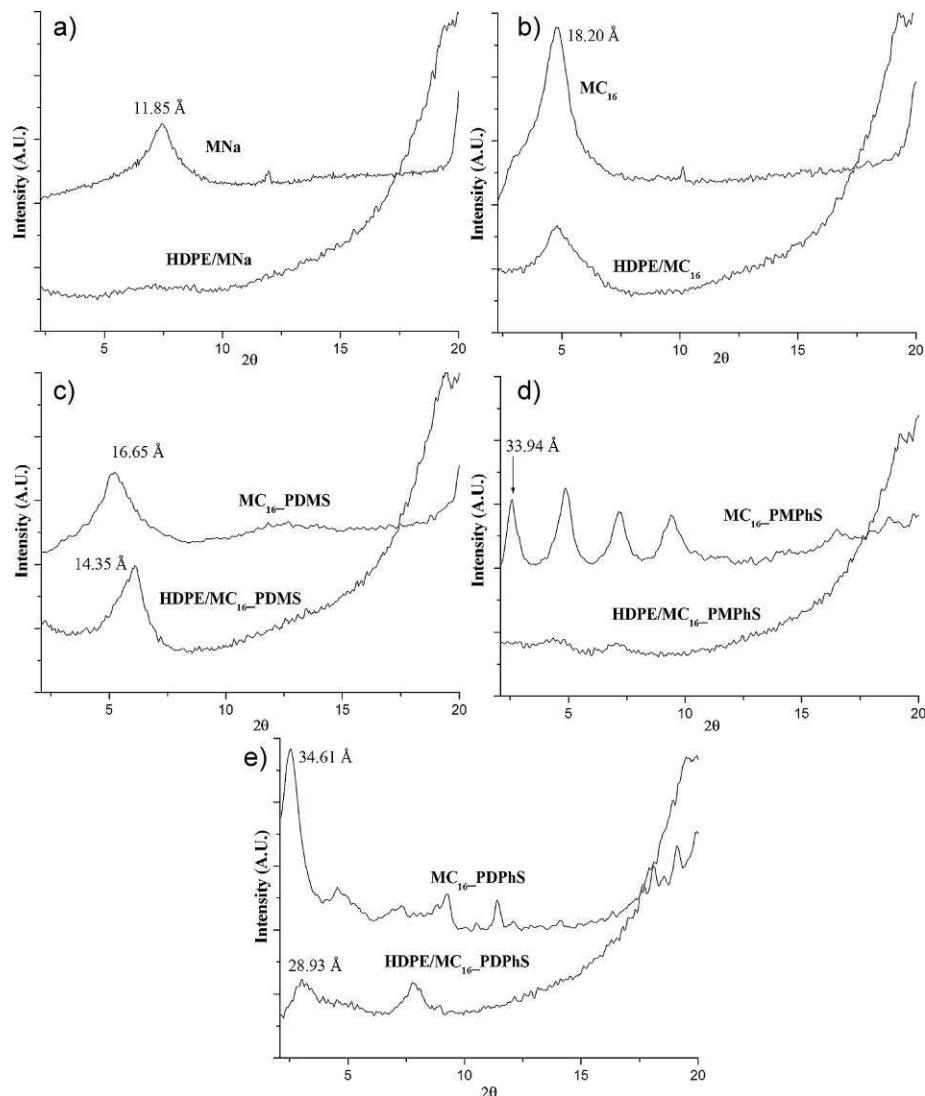
While this would suggest that DMS does not intercalate into MC<sub>16</sub>, it must be pointed out that during the preparation of these materials the same diffusive behavior was observed for the three species. This indicates that the expansive effect of the synthesis of PDMS oligomers is lower than those from the other oligomers, which may be related to the small size of DMS side groups and to the decrease in Si-CH<sub>3</sub> bond rigidity compared with Si-C<sub>6</sub>H<sub>5</sub> bond in MPhS or DPhS.

As regards XRD of clay/polymer hybrids, peak intensity decreases may be due to the dilution of additives when added to HDPE matrix, or can reflect the decrease on tactoid size.<sup>[4]</sup> Peaks have almost disappeared on Figure 1d for HDPE/MC<sub>16</sub>\_PMPHs hybrid, which indicates that the filler was dispersed in HDPE matrix. Figures 1c and 1e show HDPE/MC<sub>16</sub>\_PDMS and HDPE/MC<sub>16</sub>\_PDPhS patterns, respectively. A partial stacking recovery<sup>[18]</sup> was noticed as interlayer distances decreased, if they are compared with those of modified clays. These different behaviors can be associated with siloxane oligomeric species generated among clay platelets during hydrolysis. Two aspects must be taken into account when analyzing silane treated clays: 1) although reaction conditions were the same, each monomer generates chains of different lengths (Table 2); and 2) the chemical nature of organic groups attached to the silicon atom is different. Both factors can affect subsequent clay/polyolefin interactions.

Finally, it is necessary to point out that the absence of peaks in HDPE/MNa pattern (Figure 1a) is due not to an exfoliation, but to a dilution effect. This material has been previously studied by TEM<sup>[16]</sup> proving that no intercalation and/or exfoliation took place owing to the poor compatibility between pristine clay and HDPE.

### FT-IR Spectra Analyses

Table 3 shows the peaks observed for the additives obtained from MNa clay. Pristine



**Figure 1.**  
XRD patterns of clays and their corresponding HDPE hybrid.

clay presents the typical bands observed for montmorillonite clay.<sup>[19]</sup> The peaks corresponding to methylene group ( $\sim 2920\text{ cm}^{-1}$ ,  $\sim 2850\text{ cm}^{-1}$ ,  $\sim 1475\text{ cm}^{-1}$ ) evidence the presence of alkyl chains on MC<sub>16</sub> and siloxane treated clays.<sup>[20]</sup>

In particular, MC<sub>16</sub>\_PDMS and MC<sub>16</sub>\_PMPHS spectra exhibit absorption bands corresponding to methyl group near to  $2960\text{ cm}^{-1}$  and  $1260\text{ cm}^{-1}$ . While MC<sub>16</sub>\_PMPHS and MC<sub>16</sub>\_PDPHS spectra showed peaks corresponding to phenyl

group in the  $3100\text{--}3000\text{ cm}^{-1}$  region. This group has also presented absorption bands at  $1591\text{ cm}^{-1}$ ,  $1429\text{ cm}^{-1}$ , and between  $2000$  and  $1700\text{ cm}^{-1}$ . From these data, it was confirmed the presence of the siloxanes oligomeric species described on Table 2.

No bands near  $3440\text{ cm}^{-1}$  and  $1640\text{ cm}^{-1}$  were detected for MC<sub>16</sub>\_PMPHS and MC<sub>16</sub>\_PDPHS, evidencing their high hydrophobicity. It is important to state that  $-\text{OH}$  stretching belongs only to absorptions on the clay sheet for MNa and MC<sub>16</sub>. How-

**Table 2.**

Data obtained from GPC analyses.

Smallest basic unit	m <sup>a)</sup>	Mn <sup>b)</sup>	Polydispersity <sup>c)</sup>	DP <sup>d)</sup>
	74	375	1.10	~5
	136	392 73,100	1.32 2.37	~3 ~537
	198	331	1.26	~2

<sup>a)</sup>m = repeating unit molar mass [g/mol]<sup>b)</sup>Mn = number average molecular weight<sup>c)</sup>Polydispersity = weight average molecular weight/ number average molecular weight (Mw/Mn)<sup>d)</sup>DP = degree of polymerization (Mn/m)

ever, they also may correspond to terminal silanol groups in the case of MC<sub>16</sub>\_PDMS, MC<sub>16</sub>\_PMPHS and MC<sub>16</sub>\_PDPhS.

### Thermal Properties

Table 4 summarizes the information extracted from TG thermograms on the

final weight losses and the typical temperatures for thermal decomposition process.

In all cases, additives caused a delay on the onset compared with HDPE thermal degradation. Specifically, the hybrid containing MC<sub>16</sub>\_PMPHS presents the lowest temperature to T(1%) while the Tonset is

**Table 3.**Infrared Absorption for MNa, MC<sub>16</sub> and siloxanes-treated clays (Frequencies in cm<sup>-1</sup>)

	MNa	MC <sub>16</sub>	MC <sub>16</sub> _PDMS	MC <sub>16</sub> _PMPHS	MC <sub>16</sub> _PDPhS
—OH stretching	3621	3621	3622	3626	3620
—OH stretching	3448	3434	3437		
aromatic C—H stretching				3100 to 3000	3100 to 3000
CH <sub>3</sub> asymmetrical stretching			2966	2960	
CH <sub>2</sub> asymmetrical stretching		2922	2926	2922	2924
CH <sub>2</sub> symmetrical stretching		2850	2852	2852	2852
Combination bands				2000 to 1700	2000 to 1700
H—O—H deformation	1636	1637	1637		
C—C stretching within the ring				1591	1591
CH <sub>2</sub> scissoring band		1473	1473	1473	1475
C—C stretching within the ring				1429	1429
Si—CH <sub>3</sub> symmetric deformation			1263	1259	
Si—O in plane stretching	1035	1036	1033	1039	1035
C—H out of plane bending				729	740

**Table 4.**

Information obtained from TG curves.

Samples	T (1%) [°C]	T (10%) [°C]	Tonset	T (50%) [°C]	T (90%) [°C]	Char Yield <sup>a)</sup> [%]
HDPE	295.11	422.75	429.58	450.56	467.55	0.32
HDPE/MNa	382.94	443.54	451.60	465.49	477.21	2.42
HDPE/MC <sub>16</sub>	356.88	445.00	450.46	459.93	467.83	2.50
HDPE/MC <sub>16</sub> _PDMS	301.55	420.41	442.95	465.39	483.72	2.26
HDPE/MC <sub>16</sub> _PMPHS	270.22	451.74	463.68	477.41	489.79	1.69
HDPE/MC <sub>16</sub> _PDPHS	315.31	450.27	457.00	469.10	479.48	1.96

<sup>a)</sup>Values differ from those expected evidencing dispersion defects.<sup>[21]</sup>

the highest. These results can be associated with the bimodal behavior of oligomers extracted from this modified clay. At the beginning there is a weight loss even lower than HDPE which matches the existence of species with a lower molecular weight. Then PMPHS oligomers with higher molecular weights participate later reaching the highest onset temperature for this material which is Tonset.

When 10% of weight loss is reached, HDPE/MC<sub>16</sub>\_PDMS exhibits similar values of temperature close to pure polymer. HDPE/MC<sub>16</sub>\_PMPHS and HDPE/MC<sub>16</sub>\_PDPHS show the highest temperatures if compared with the rest of hybrids. Mixtures containing MNa and MC<sub>16</sub> show similar values between them.

While weigh loss increases HDPE/MC<sub>16</sub>\_PMPHS hybrid presents the highest temperature values. At 90% weight loss, composites containing additives modified by siloxanes show the highest temperatures.

Table 4 presents values obtained from TGA and DTG curves. According to Van Krevelen, the ratio T<sub>max</sub> ~ T<sub>50%</sub> is applicable to these results.<sup>[22]</sup> However, the other ratios proposed by this author referred to activation energy and initial weight loss temperatures are not kept.

Activation energy values were calculated by taking into account first-order kinetics. Arrhenius equation was used:

$$\ln\left(-\frac{1}{m} \cdot \frac{dm}{dt}\right) = \ln A - \frac{E_a}{RT}$$

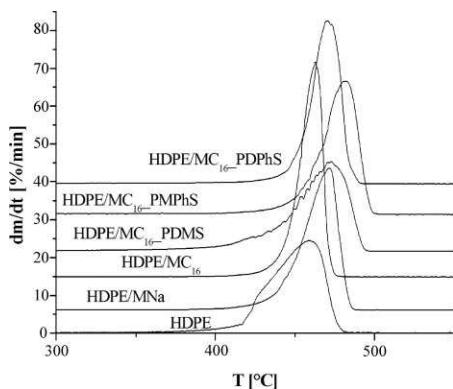
Although HDPE shows first-order kinetics, it exhibits two activation energies.<sup>[24]</sup> This is associated with the fact that for low

weight losses, the degradation is related to imperfections on polymer chains and the elimination of high volatile products. But the second degradation stage involves C–C bond ruptures that implicate more energy.<sup>[25,23]</sup> Several authors have researched on this polymer and report different energy values and reaction orders.<sup>[23]</sup>

In this work, the introduction of modifiers to polymer matrix in all cases causes changes on activation energy values evidencing alterations on the degradation process, compared with pure polyolefin.

It is well known that polyolefin decomposition process mainly occurs through a random chain rupture, and not by depolymerization. The activation energy calculated involves a complex mechanism which should consider two aspects: i) typical reaction characteristics of solid-gas systems via free radical, and ii) chain reactions. The first ones are affected by the spreading of the reaction volatile products, which is related to the nanoplatelet dispersion within the HDPE, and the latter are affected by the chain reaction mechanisms.<sup>[26,10]</sup> As studied hybrids have had the same polymer matrix, it can be concluded that additives used have caused different effects on this mechanism, and for that reason different behaviors had been observed. Although nanoclay effect was mentioned, it is obvious that is not the only factor that affects these behaviors.

DTG curves (Figure 2), activation energies and maximum mass loss rate (Table 5) exhibit similar tendencies among some materials. In the first stage of degradation, hybrids modified by sodium clay and MC<sub>16</sub> have higher thermal stabilities as

**Figure 2.**

DTG curves of prepared materials.

they presented an increase on Ea<sup>[23]</sup> compared with pure HDPE values, but composites modified by siloxanes presented lower Ea values. This is probably due to the fact that siloxane systems contain oligomeric species (verified by GPC), which may be eliminated from each system more easily during heating. As regards the second stage, activation energies were higher which means that fillers have had a stabilization effect, except for HDPE/MC<sub>16</sub>\_PDMS.

Finally after analyzing maximum rate of degradation, polymer containing MC<sub>16</sub>\_PMPHs as modifier presents the maximum mass loss rate, at 20 °C over pure HDPE,

and HDPE/MC<sub>16</sub>\_PDMS shows the lowest value.

### Barrier Properties

Permeability values and the permeation activation energies (EaP) for each HDPE/clay hybrid are described in Table 6. Composites containing MNa and MC<sub>16</sub>\_PDMS show enhanced barrier properties with respect to pure HDPE.

If EaP values are compared to interlamellar spaces (Figure 1) there is no correlation between these factors. This may be inferred after consideration of HDPE/MC<sub>16</sub> and HDPE/MC<sub>16</sub>\_PDMS values. Even though clay gallery heights are similar, EaP are quite different. Thus, polymer intercalation degree is not the only factor that influences barrier properties.

EaP involves several aspects. On the one hand, it indicates temperature sensibility of each system (membrane). It was observed that permeation process is more influenced by temperature for HDPE/MNa and it is barely affected for HDPE/MC<sub>16</sub>\_PMPHs. On the other hand, EaP involves information about solubility and solvent diffusion through membrane.<sup>[27]</sup> Then, it is evident that both processes were changed by species used as MNa modifiers.

Although fillers are well dispersed as shown SEM microphotographs (Figure 3),

**Table 5.**  
Data obtained from themogravimetical analyses.

Samples	Max. Mass loss rate [%/min] <sup>a)</sup>	T <sub>max</sub> [°C] <sup>a)</sup>	Ea [kJ/mol] <sup>b)</sup>	ΔT [°C] <sup>c)</sup>
HDPE	24.52	458.99	71.61 332.32*	315–405 405–480
HDPE/MNa	37.41	471.52	155.84 498.79	390–430 430–480
HDPE/MC <sub>16</sub>	56.77	462.80	108.02 636.37	360–440 440–465
HDPE/MC <sub>16</sub> _PDMS	23.57	472.82	64.40 255.66	290–375 375–475
HDPE/MC <sub>16</sub> _PMPHs	35.17	481.73	62.25 460.56	275–415 415–480
HDPE/MC <sub>16</sub> _PDPHs	43.21	470.37	40.68 527.71	310–420 420–475

<sup>a)</sup>Temperature at maximum mass loss rate<sup>b)</sup>Activation energy (Ea) calculated according to TGA curves<sup>c)</sup>Temperature range for Ea calculations\*Value similar to that reported by Albano et al.<sup>[10]</sup> and Chrissafis et al.<sup>[23]</sup>

**Table 6.**

Results extracted from pervaporation at different temperatures.

Sample	T = 50 °C		T = 60 °C K		T = 70 °C		EaP [kJ/mol]
	P <sup>a)</sup>	P <sub>R</sub> <sup>b)</sup>	P	P <sub>R</sub>	P	P <sub>R</sub>	
HDPE	129.99	1.00	151.12	1.00	221.57	1.00	24.44
HDPE/MNa	77.84	0.60	145.39	0.96	196.05	0.88	42.68
HDPE/MC <sub>16</sub>	148.13	1.14	154.31	1.02	205.65	0.93	14.99
HDPE/MC <sub>16</sub> _PDMS	79.35	0.61	124.47	0.82	173.22	0.78	36.00
HDPE/MC <sub>16</sub> _PMPHs	173.23	1.33	181.36	1.20	185.43	0.84	3.14
HDPE/MC <sub>16</sub> _PDPhS	131.45	1.01	184.27	1.22	232.57	1.05	26.32

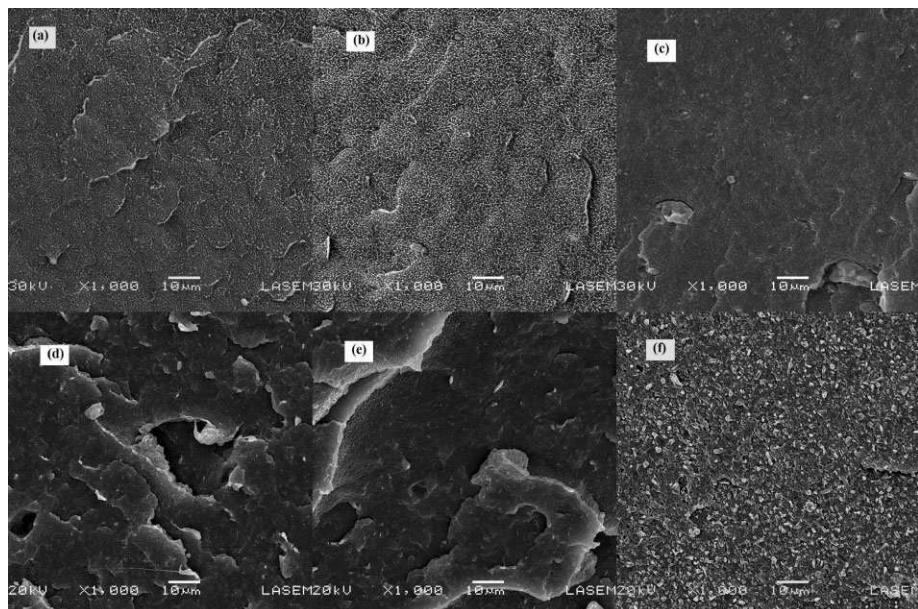
<sup>a)</sup>p in [g.mm/day · m<sup>2</sup> · atm]<sup>b)</sup>P<sub>R</sub> = Relative permeability = P/P<sub>HDPE</sub><sup>c)</sup>ε<sub>sheet</sub> = 9.5 Å

different morphologies are observed according to the additive used. This is intimately related to changes observed on macroscopic properties.

The highest EaP of HDPE/MNa can be associated to the low interaction polymer/clay, which becomes more marked as temperature increases. This will lead to greater mobility of HDPE chains which will promote interface separation and consequently the free volume will increase facilitating cyclohexane diffusion. Tempera-

ture sensibility, i.e. EaP, is lower for HDPE/MC<sub>16</sub>\_PDMS, probably due to an improvement of interface contact caused by the presence of –CH<sub>2</sub> from alkyl chains and –CH<sub>3</sub> groups from PDMS oligomers.

Activation energies for HDPE/MC<sub>16</sub> and HDPE/MC<sub>16</sub>\_PMPHs have decreased significantly taking pure HDPE as reference. In the first case, it is evident that the hydrophobicity of alkyl chains was not enough to avoid free volume increase during cyclohexane transport. In the second, the

**Figure 3.**

SEM microphotographs of (a) HDPE,<sup>[16]</sup> (b) HDPE/MNa, (c) HDPE/MC<sub>16</sub>, (d) HDPE/MC<sub>16</sub>\_PDMS, (e) HDPE/MC<sub>16</sub>\_PMPHs and (f) HDPE/MC<sub>16</sub>\_PDPhS.<sup>[16]</sup>

increase in free volume is not due to the lack of compatibility, as can be inferred from XRD patterns (Figure 1d). Nevertheless, PMPhS oligomers (Table 2) have a large length; consequently they can separate HDPE chains.

Finally, HDPE/MC<sub>16</sub>\_PDPhS exhibits similar EaP and permeabilities than pure HDPE. By means of Figure 1e, it can be observed that HDPE partially intercalates due to the high distance generated for the presence of the bulky groups from DPhS. However, the dimers obtained (Table 2) seem not to influence the original free volume of HDPE.

## Conclusion

In this work, a natural multilayer clay mineral was used as raw material. Hydrophilic clay was modified at nanometric level by the introduction of species with different chemical functionalities, in order to obtain additives for HDPE. Three modified clays were synthesized containing siloxane oligomers with different behaviors.

Macroscopic changes have taken place on HDPE after its hybridization with synthesized nanomaterials. According to XRD results, HDPE/MC<sub>16</sub>\_PMPhS exhibited an intercalated/exfoliated structure while others HDPE/clay hybrids have shown microcomposite structure. Nonetheless, after evaluating thermal and barrier properties, their responses did not follow a direct correlation with the degree of intercalation.

Resistance to thermal non-oxidative degradation was improved when siloxane-modified clays or pure clay were used. Concerning barrier properties, HDPE/MNa and HDPE/MC<sub>16</sub>\_PDMS have shown better results in terms of cyclohexane permeability at low temperatures. Meanwhile, HDPE/MC<sub>16</sub>\_PMPhS was the hybrid with the lowest EaP.

Thus, it was concluded that HDPE macroscopic properties were mainly influenced by the interactions existing between the polyolefin and clay surface modifiers.

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# Ballistic Performance and Damage Characteristics of Chemical Vapor Infiltration Quasi 3D-Cf/SiC Composites

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**Abstract:** To investigate the ballistic performance and damage characteristics of quasi three-dimensional (3D) needle-punched Cf/SiC composites prepared by chemical vapor infiltration (CVI), penetration experiments were conducted by using 7.62 mm armor piercing incendiary (API). Macro and micro fracture morphologies were then observed on recycled targets. The results show that the protection coefficient of 3D Cf/SiC composites is 2.54. High porosity and many micro thermal stress cracks may directly lead to the lower ballistic performance. Flat fracture morphology was observed on the crater surface. The low dynamic fracture strength along layer direction may be attributed to the voids and microcracks caused by residual thermal stress. The damage characteristics of Cf/SiC composites include matrix cracking, fiber bundle cracking, interfacial debonding, fiber fracture, and fiber bundle pull-out. And interfacial debonding and fiber fracture may play major roles in energy absorption.

**Key words:** CVI-Cf/SiC; composites material; ballistic performance; damage characteristics

## 1 Introduction

With rapid development of anti-armor weapons technology, armors are in competition with projectiles. It is desirable that the armor should be able to withstand the projectile by itself. It can be regarded as a yardstick to measure the armor's performance<sup>[1]</sup>. In order to improve the protection performance and battlefield survivability of the armor so that it can effectively resist the AP and HEAT, the armor protection materials have developed toward strengthening, toughening and light weight.

Traditionally, armor materials were high hardness steel. However, the demand for lightweight armor has led to the investigation of the ceramic materials. Due to low density, high hardness, high rigidity and high strength in compression, ceramic has been widely applied to armors<sup>[2-6]</sup>. However, the low fracture toughness of the ceramics has severely limited their application and led to the development of the ceramic

matrix composite materials. Cf/SiC ceramic matrix composites have such advantages as high temperature resistance, high wear resistance, high strength, high toughness, high hardness and low density, all of which enable them to be considered as desirable high temperature structure materials, especially in light weight armor protection field<sup>[7]</sup>.

Because of subjecting to impact loads in service processes, study on the dynamic mechanical properties of the armor materials is very important. At present, the responses of Cf/SiC composites under dynamic impact condition have been studied by many domestic institutions. Liu Mingshuang<sup>[8]</sup> investigated the dynamic compressive properties of 2D Cf/SiC at strain rate ranging from  $10^{-4}$  to  $2.8 \times 10^3 \text{ s}^{-1}$  with the split hopkinson pressure bars (SHPB) system. From the results, the dynamic compressive stress-strain curves are non-linear and the failure strain reduces with increasing strain rate. Besides, the scatter of dynamic compressive failure strength obeys the Weibull distribution. Wang Yingchun et al<sup>[9]</sup> improved the SHPB using the pulse shaper to investigated the 2D Cf/SiC, and they found that the composite exhibits higher strength and better ductility at elevated temperature in the range of 460-500 °C. The dynamic compressive mechanical behavior of a quasi-3D needle-punched Cf/SiC composite at room temperature was investigated

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at strain rate ranging from  $10^{-4}$  to  $6.5 \times 10^3 \text{ s}^{-1}$  using SHPB by Li Yulong *et al*<sup>[10,11]</sup>, who reported that the strain rate has slight influence on the mechanical property of the material, and the dynamic compression strength obeys the Weibull distribution too.

However, the ballistic performance and damage characteristics of the 3D-Cf/SiC composite under target impact conditions have not been reported yet.

In this paper, target experiments with 7.62 mm armor piercing incendiary were conducted on the chemical vapor infiltration quasi 3D-Cf/SiC composites. The macro and micro damage morphologies were investigated using scanning electron microscopy (SEM) and the damage characteristics was analyzed.

## 2 Experimental

### 2.1 Materials

The quasi 3D-Cf/SiC composites tested in this study were offered by the State Key Laboratory of Solidification Processing in Northwestern Polytechnical University, People's Republic of China. The performs were firstly prepared by three dimensional needle punch. Then isothermal CVI was employed to deposit a pyrolysis carbon layer on the surface of carbon fiber about 0.1-0.2  $\mu\text{m}$  thickness. Finally, SiC matrix was deposited by CVI to get the composite<sup>[12]</sup>.

### 2.2 Ballistic experiment

In order to approach real service environment and get higher penetration velocity, target experiments were performed with 7.62 mm armor piercing incendiary (API) in the indoor range of armour piercing laboratory of No.52 Institute of China Weaponry Industrial Group. The distance between the armor and running position of the projectiles was 8 m. The velocity of the 7.62 mm projectiles was 820 m/s. The target was vertical layout and stucked to the back of 45 steel whose thickness was 25 mm. The size of 3D-Cf/SiC composites used in this investigation was 50 mm×50 mm×10 mm.

Depth of residual penetration (DRP) was employed to evaluate the relative protection performance between armors. What's more, the mass efficiency ( $E_m$ ) and the differential efficiency factor ( $e_f$ ) were adopted to characterize the ballistic performance of the composite targets. This value represents the factor by which mass per area must be multiplied if

an entire armor combination, consisting of a ceramic thickness and a steel back-up thickness was to be replaced by homogeneous steel for equal protection against AP<sup>[13]</sup>.

The expression is:

$$E_m = \frac{P\rho_s}{T\rho_c + P_r\rho_s} \quad (1)$$

$$e_f = \frac{(P - P_r)\rho_s}{T\rho_c} \quad (2)$$

where  $\rho_s$  is the density of homogeneous steel target and  $\rho_c$  is the density of composite target.  $P$  is the penetration depth of homogeneous steel, while  $P_r$  is the residual penetration depth of the backplane of composite target.  $T$  is the thickness of composite target.

### 2.3 Microstructural observation and analysis

In this study, failure mechanisms and damage behaviors of the composites were observed under impact loading conditions. Macro-examinations of the damage zone were also conducted by photography. For microstructural analysis, the samples were cut with the wire-electrode cutting in appropriate dimensions. In order to observe the failure mechanisms resulting from the ballistic impact event, OM and SEM studies were also performed.

## 3 Results and discussion

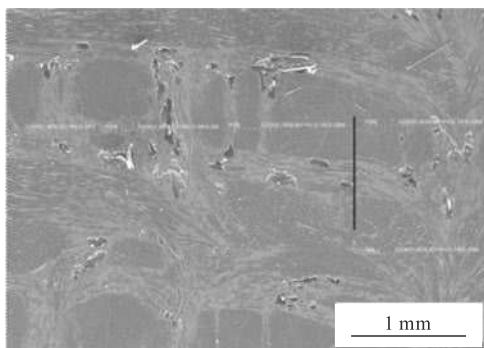
### 3.1 Microstructure characterization and mechanical properties

The microscopic morphologies of the 3D-Cf/SiC composite can be seen in Fig.1(a) and Fig.1(b). Two kinds of pores with different shapes and sizes were found within the materials: one was the large pore between fiber bundle and matrix (shown in Fig.1(c)), and the other was the small pore between fiber and fiber within the fiber bundle (shown in Fig.1(d)). The sizes of both kinds of pores were in the millimeter and micrometer scale respectively. Because these pores existed with the fiber and fiber bundle in the composites, the pores were tortuous and elongated. In addition, due to the mismatch of thermal expansion coefficients between matrix and reinforcement, a large number of microcracks were formed because of residual thermal stress. In a word, there were a lot of defects in the composites. These defects were arrested

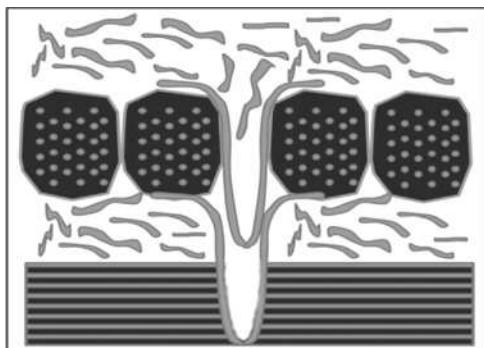
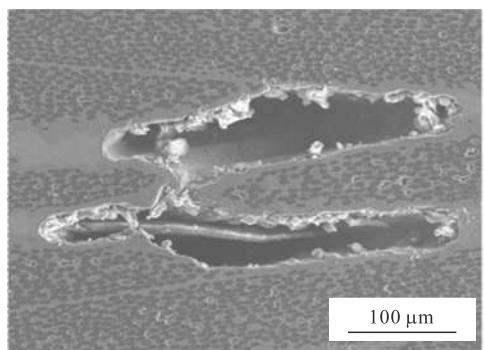
Table 1 Mechanical properties of the 3D-Cf/SiC composite

Porosity /%	Density/(g/cm <sup>3</sup> )	Volume fraction/%	Shear strength/MPa	Tensile strength/MPa	Compressive strength/MPa	Bending strength/MPa	Fracture toughness /MPa·m <sup>1/2</sup>
5.2	2.16	32	105	121	596	455	16

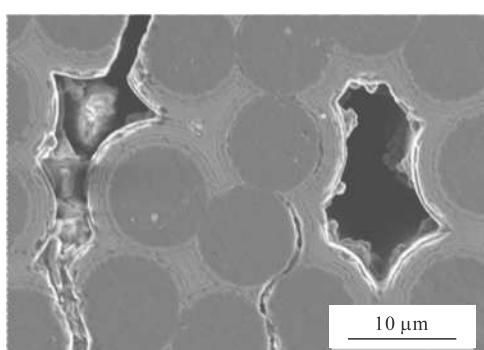
under the pressure stress condition. On the contrary, they were induced under the tensile stress condition. Therefore, the tensile modulus of the composite was lower than the compressive modulus. Similarly, the tensile strength was also lower than the compressive strength. The mechanical properties of this composite are shown in Table 1.



(a) 3D Cf/SiC morphology

(b) 3D Cf/SiC structure model<sup>[12]</sup>

(c) Pore between the fiber bundles



(d) Pore in the fiber bundles

Fig.1 Microscopic morphologies of the Cf/SiC composite

### 3.2 Ballistic performance of the composites

The target experiments' results are shown in Table 2. It can be seen that the  $E_m$  and  $e_f$  of three specimens are 1.30, 1.16, 1.23 and 2.91, 2.18, 2.54, respectively. Thus, the average  $E_m$  and  $e_f$  of the composite target are 1.23 and 2.54.

Table 2 Result of the target experiments

No.	1	2	3	4
$P$	23	—	—	—
$P_r$	—	15	17	16
$E_m$	—	1.30	1.16	1.23
$e_f$	—	2.91	2.18	2.54

### 3.3 Damage characteristics of the target

On the basis of recovering fragment behind the target, the damage phenomena of the 3D-Cf/SiC composites were studied. Three targets were broken in the same fracture mode. It is shown that crushing failure happens in the vicinity of the impact region. Fracture damage was the heaviest in a region directly beneath the impact site. However, the materials away from the crater of the position kept a good integrity. A circular crack initiated near the impact point; while a few radial tensile cracks initiated at the front surface close to the impact point.

The crushing effect of the projectile caused a big crater, resulting from the breaking of the brittle composite layer. It is obvious that the layer was broken into pieces, and the crack fracture direction was parallel to the projectile impact direction. So flat fracture took place during the ballistic impact. The needle integrated felts were prepared by the three dimensional needling technique, starting with repeatedly overlapping the layers of 0° non-woven cloth, short-cut fiber web, and 90° non-woven fiber cloth with needle punching step by step (shown in Fig.1(b)). So the thermal stress distributed unevenly inside the material. The defects were concentrated. The crack could pass through these defects easily. Although the horizontal fiber bundle could change the crack direction, the existence of the defects made the distance of the deflecting crack short. The fiber bundle fracture prematurely made the fracture surface broken flatly.

Under the condition of projectile impact, when either a dilatational or a distortional wave impinges on a boundary of the solid, waves of both tensile and compressive types are generated. The pulse is reflected from the back of target or a free surface as a tensile wave and if its magnitude is greater than the dynamic tensile fracture strength of the material, fracture will occur.

The 3D-Cf/SiC performs were prepared with layered fiber. In the CVI process, the SiC matrix was firstly deposited on the surface of carbon fiber, then

on the surface of the fiber bundle. The amount of infiltration was dependent on the size and geometry of the pores. Due to limitation of the CVI process and structure complexity of fibers, it was very difficult to fully fill the pores. When the deposition process could not fill the pores within layered fiber, the pores were left. It is well known that residual pores in the material can be considered as a kind of defects and may act as failure source. The strength would decrease because the effective bearing volume of the materials decreased with the increase of the pores. On the other hand, the junction between the fiber and the matrix was the place where thermal stress concentrated. All the above factors would lead to the low tensile strength of the layer in the material. When the applied stress exceeded the dynamic fracture strength, the spall would be produced in the target.

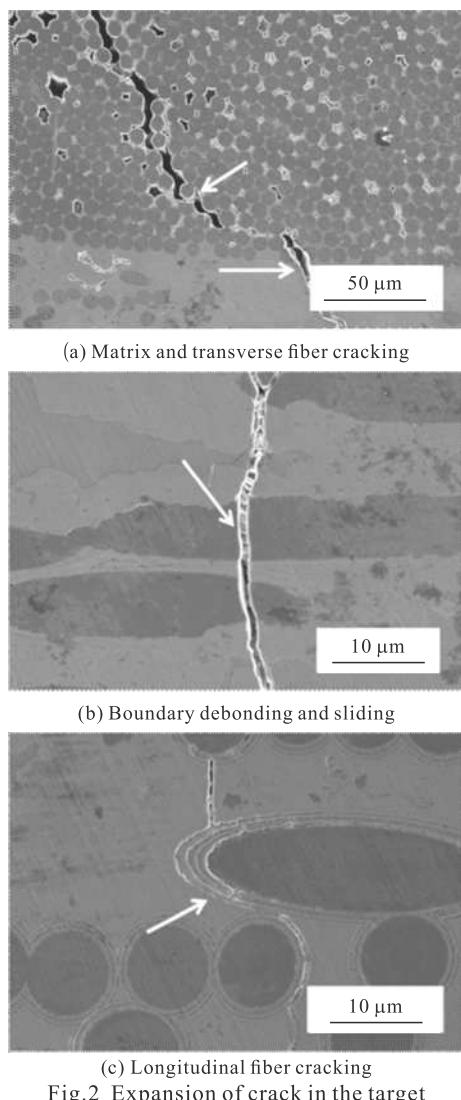


Fig.2 Expansion of crack in the target

Due to the low tensile strength of the matrix phase, the crack would generate and spread firstly (shown in Fig.2(a)). The matrix fractured in brittle

mode. The low adhesion of the boundary between the brittle fiber and brittle matrix made the crack deflect its direction, so the debonding and sliding of the boundary were created (shown in Fig.2(b)). With the increase of stress, the crack would extend along the pore in the transverse fiber bundle easily, which made the fiber bundle dehisced. When the crack was produced and extended under the impact condition, it could pass through longitudinal (90°) fiber bundles easily. And only horizontal (0°) fiber bundles along the force direction of the length could prevent propagation and deflect the crack effectively (shown in Fig.2(c)).

With the increase of stress, the crack density reached saturation, but the matrix stress could not increase with the external load any more. Thus the applied stress was mainly born by the carbon fiber. With the continuous increase of stress, the fiber began to break. When the stress reached the maximum tensile strength, the damaged fiber bundle was unable to withstand the load and then pulled out from the matrix, which made the fracture surface look rough. Generally, fracture behavior of fiber is dependent on the interface bonding between fiber and matrix. If interface bonding is strong, fiber may break. While, fiber may pull-out if interface bonding is weak (shown in Fig.3).

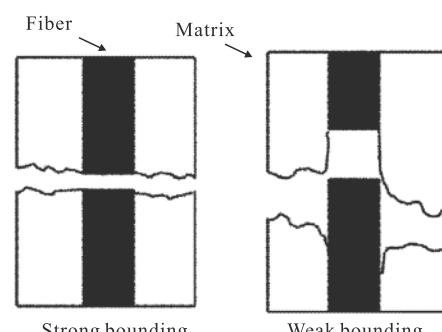


Fig.3 Fracture behavior of fiber

Micro structural observations revealed that the failure behavior of composites was dominated by fiber fracture, fiber pull-out and fiber bundle pull-out damage mode (shown in Fig.4). If less SiC matrix was deposited in the texture, it would lead to weak bonding between fiber bundle and bundle. So fiber bundle would be pulled out rather than break (Fig.4(a)). As bonding strength increased with the amount of deposited matrix, it would give rise to brittle fracture and catastrophic damage (Fig.4(b)). Sometimes, there was not only fiber pull-out but also brittle failure of the sub-bundle (Fig.4(c)).

Obviously, the results revealed that the composite will have suitable interface bonding strength if the Pyc layer has a moderate thickness. In other words, the interface should not only be strong enough to allow

load transfer from the matrix to the fiber under stress, but also weak enough so that an advancing matrix crack can be deflected by the fiber. For the 3D-Cf/SiC composite material target, good toughness is achieved by the appropriate interface which acts as a mechanical fuse by deflecting the matrix cracks. On the other hand, the existence of the pores in the material may decrease the Young modulus of the matrix, which may result in the weak interfacial bounding strength. From the macro point of view, the SiC matrix which is deposited between the fiber bundles rather than inside them creates favorable conditions for the whole fiber bundle pull-out. All the above reasons finally result in the fiber bundle pull out easily.

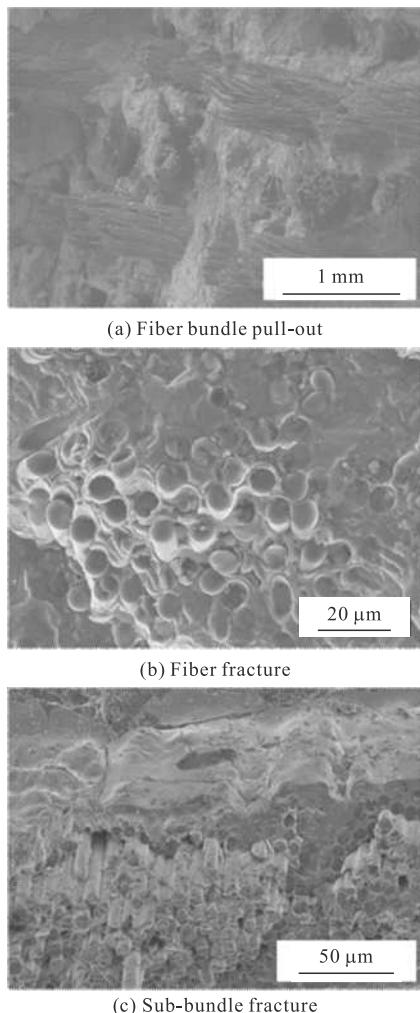


Fig.4 Microscopic morphologies of the fiber fracture

Under impacting condition, the internal tensile stress in the target increases to the fracture strength of the material instantaneously and makes the target fracture into pieces. The material exhibits matrix cracking, fiber bundle cracking, interfacial debonding, fiber fracture, fiber bundle pull-out and other fracture models. When the stress increases to a certain level in a short period of time, these fracture models occur

in turn. The target crushes finally. Besides, the impact is weak in the places far away from the crater, so the target in these places maintains integrity. The destructive process involves multiple energy absorption mechanisms. And interface debonding and fiber pull-out are the main damage characteristics.

## 4 Conclusions

a) Under target penetration experiments, the mass efficiency ( $E_m$ ) and the differential efficiency factor ( $e_f$ ) of 3D-Cf/SiC composites are 1.23 and 2.54 respectively. Higher porosity and a large number of microscopic thermal stress cracks are the fundamental causes of the low ballistic performance.

b) The crater playing surfaces of the 3D-Cf/SiC targets present damage morphologies of plane form flat fracture. Owing to voids and microcracks caused by residual thermal stress, the dynamic fracture strength of layered fiber is low.

c) The failure mechanisms of 3D-Cf/SiC composite targets include matrix cracking, fiber bundle cracking, interfacial debonding, fiber fracture, fiber bundle pull-out and other damage characteristics. Additionally, interfacial debonding and fiber fracture play the major roles in energy absorption.

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What is This?

# The surface modification of ballistic textiles using plasma-assisted chemical vapor deposition (PACVD)

**MH Struszczyk<sup>1</sup>, AK Puszkarz<sup>2</sup>, B Wilbik-Hałgas<sup>1</sup>, M Cichecka<sup>1</sup>,  
P Litwa<sup>1</sup>, W Urbaniak-Domagała<sup>2</sup> and I Krucinska<sup>2</sup>**

## Abstract

This paper describes studies on the surface modification of so-called ballistic materials (materials commonly used to protect the human body against firearms, i.e. fragments or bullets). Two materials, an ultra-high molecular weight polyethylene (UHMWPE) composite and aramid fabric, were investigated. The surfaces of these fibrous materials were modified using plasma-assisted chemical vapor deposition (PACVD) to examine the effects of the modification on the material properties, which are important for designing ballistic protections. Accordingly, both the mechanical strength and water resistance of the modified materials were tested. The results clearly show the impact of the modification on both parameters.

## Keywords

surface modification, material strength, material properties, PACVD, chemical modification, composites

Over the last 20 years, most of the literature reports on the modification of ballistic material surfaces by plasma-assisted chemical vapor deposition (PACVD) have focused on the modification of basic raw materials—fibers, yarns or purified fabrics.<sup>1–6,8</sup> Experiments on these materials focused on improving the adhesion (e.g. of ultra-high molecular weight polyethylene (UHMWPE) to epoxy resin or low-molecular weight polyethylene as a ballistic material matrix).<sup>12,13</sup> Improved adhesion allows the modified fibers and matrix to form a more stable connection.

Low-temperature plasma techniques are superior to the currently used finishing techniques because they do not require large quantities of water or toxic processing aids and are therefore more environmentally friendly. Additionally, the plasma modification process is significantly more efficient economically and technologically than standard dyeing and finishing processes. In a relatively short time, the surface properties of the material can be significantly altered in a controlled manner to improve the wetting, adhesion, oleophobic resistance or superhydrophobicity, changing the physical characteristics, or to sanitize and disinfect the large surfaces of the materials.<sup>9</sup>

Moreover, the modification of aramid fibers with NH<sub>3</sub> plasma and O<sub>2</sub> plasma was studied. The application of these two gases improved aramid fiber adhesion to epoxy resin without significantly affecting the mechanical strength (approx. 10%).<sup>7</sup> Additionally, the effects of modifying purified aramid fabrics with plasma on pre-impregnates constructed from the modified fibers and phenol resin were investigated.<sup>10</sup> The structural changes in the aramid fibers due to the plasma modification were investigated with XPS and FT-IR, and their morphology was examined with SEM. During the fiber surface modification, oxygen and hydrogen functional groups were created. As a

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result, the adhesion of the p-aramid fabric to the phenol resin improved. Additionally, resistance to abrasion and delamination of the terminal pre-impregnates (prepregs) was observed.

The use of argon in the plasma modification of UHMWPE resulted in changes in its wettability and resistance to mechanical damage at the surface. The results show that the application of this gas improved properties that are fundamental to the production of ballistic components.<sup>11</sup>

The inclusion of wool in ballistic materials can significantly improve the tear strength of pure synthetic ballistic fabrics.<sup>13</sup>

Because the fibers are fundamental elements of the final fabric structure, their surface modification resulted in abrasion during the waving process and thus led to some problems during textile fabrication. The same phenomenon was observed during the preparation of an UHMWPE fiber composite when the fibers were incorporated into the polymer matrix (polyisoprene binder and polyethylene film).<sup>12,14</sup>

Previous research focused only on the surface modification of single fibers to improve the affinity of the high-strength fibers to resin for use in the fabrication of prepregs. The structure of fibrous materials, especially fabrics or fibrous composites, is significantly more complex than that of others (i.e. films, foils). Thus, the functionalization processes for fibrous materials are more complicated, especially in terms of their consistency and durability.

The aim of this study was to investigate the effects of low-temperature plasma treatment in the presence of two low molecular mass organic derivatives containing fluorine or silicon on the most critical properties of two types of ballistic raw materials, a p-aramid woven fabric and UHMWPE fiber composite, for future applications.

## Materials and methods

This work investigated the influence of the surface modification of two different materials by PACVD on their properties (especially those critical for ballistic applications). Specifically, the materials studied were Kevlar® (p-aramid woven fabric; SAATI/Spain; surface density acc. the PN-ISO 3801:1993 Standard— $212.0 \pm 2.0 \text{ g/m}^2$ ; thickness acc. the PN-EN ISO 5084:1999 Standard— $0.20 \pm 0.02 \text{ mm}$ ) and the Dyneema® SB51 composite (ultra-high molecular weight polyethylene; DSM/The Netherlands; surface density acc. the PN-EN ISO 2286-2:1999 Standard— $251.0 \pm 2.0 \text{ g/m}^2$ ; thickness acc. the PN-EN ISO 2286-3:2000 Standard— $0.19 \pm 0.02 \text{ mm}$ ). The soft ballistic Dyneema® composite consists of a low molecular weight polyethylene (LMWPE) and polyisoprene

binder matrix that contains UHMWPE fibers.<sup>12,13</sup> The soft ballistic Dyneema® composite is composed of approx. 70 wt% UHMWPE fibers and 30 wt% LMWPE and binder.<sup>12</sup>

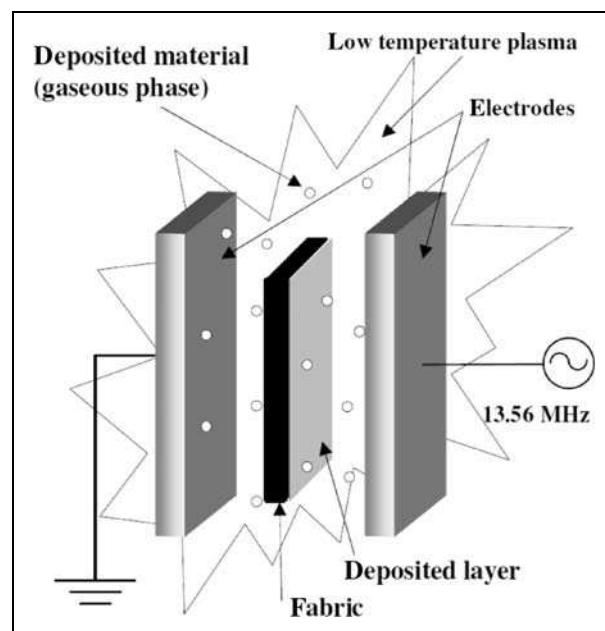
Both materials are usually used to design soft ballistic inserts for bullet- and fragment-proof vests.

The surfaces of these materials were modified using a low-temperature, radio-frequency (13.56 MHz) plasma generator as depicted in Figure 1.

The PACVD system (CD 400 PLC R/R model; Europlasma, Belgium) consisted of two parallel rectangular aluminum electrodes. The right one was connected to an alternative voltage (radio frequency—13.56 MHz), whereas the left one was grounded. The surface to be modified was placed between the electrodes, facing the right one. During the process, the material to be deposited was injected (in the gas phase) into the chamber simultaneously with the gas used for the plasma initiation.

The surface modification of both Kevlar® and Dyneema® was performed in five stages: (a) proper evacuation of the chamber, (b) surface cleaning, (c) surface activation, (d) deposition of the material on the surface, (e) conditioning of the deposited layer. The appropriate conditions (gas type, gas stream, stage duration, deposited material, chamber pressure, electric power required for the initiation and continuation of the plasma treatment, etc.) must be determined for each stage.

To modify both Kevlar® and Dyneema®, two organic compounds, namely hexamethyldisiloxane



**Figure 1.** PACVD system.

(HMDSO) ( $C_6H_{18}OSi_2$ ; molecular mass: 162.38 g/mol; Sigma Aldrich) and tetradecafluorohexane (TDFH) ( $C_6F_{14}$ ; molecular mass: 338.04 g/mol; Tokyo Chemical Industry), were used.

After the surface modification of both raw materials, their properties were measured and compared to those of the unmodified materials.

Two gases, argon and air, were used to modify the Kevlar® woven fabric surface. The process stages in which they were used are given in Table 1. For the HMDSO deposition, the compound was injected into the chamber simultaneously with argon.

Two gases, argon and air, were used to modify the Dyneema® SB51 surface. The process stages in which they were used are given in Table 1.

The mechanical resistances of the unmodified and modified surfaces were tested according to the following standards:

1. For the Kevlar® woven fabric: (a) tear resistance acc. the PN-EN ISO 13937-2:2002 Standard; (b) tensile strength and elongation at the maximum force acc. the PN-EN ISO 13934-1:2002 Standard; (c) bursting strength acc. the PN-EN 863:1999 Standard.
2. For the Dyneema® SB51 composite: (a) tear resistance acc. the PN-EN ISO 4674-1:2005 Standard; (b) tensile strength and elongation at the maximum force acc. the PN-EN ISO 1421:2001 Standard; (c) bursting strength acc. the PN-EN 863:1999 Standard.

The testing methods for the fabrics (Kevlar®) and fibrous composite materials (Dyneema®) were selected based on the material specifications in the standards for a range of applications and our experience in testing of a wide range of ballistic materials. Moreover, the testing methods selected for the Dyneema® composite allowed the real mechanical behavior of the material to be determined.

The first two tests were performed in the two perpendicular directions, namely along the warp and weft of the fabric.

Additionally, the water resistance of the materials was examined because it indirectly affects the long-term usability of ballistic products. Two parameters were evaluated: (a) the resistance to surface wetting

**Table 1.** Stages of the surface modification of the Kevlar® woven fabric and Dyneema® SB51

Deposited material	HMDSO	TDFH
Surface cleaning	Ar	Ar
Surface activation	Air	Air
Deposition	$Ar + C_6H_{18}OSi_2$	$C_6F_{14}$

(spray test) acc. the PN-EN 24920:1997 Standard and (b) the water repellency of the fabrics during the Bundesmann rain-shower test acc. the PN-EN 29865:1997 Standard. Moreover, the resistance of Dyneema® SB51 to water penetration was tested acc. the PN-EN 20811:1997 Standard.

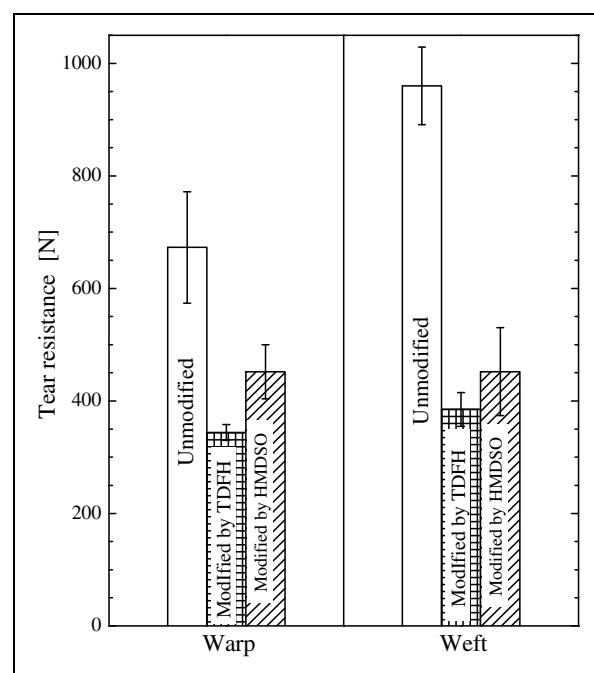
## Results and discussion

### Modification of the Kevlar® woven fabric

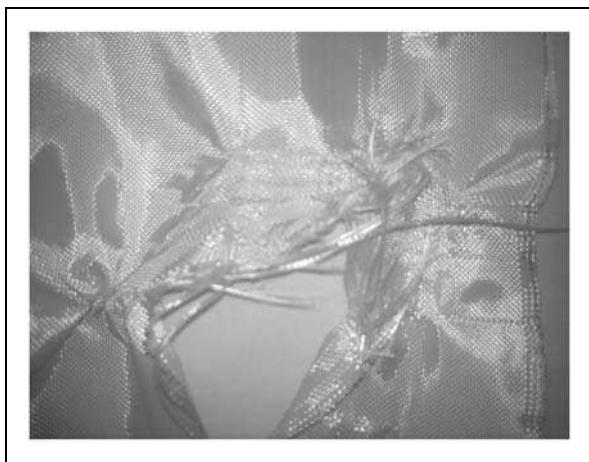
**Tear resistance.** Both HMDSO and TDFH deposition clearly result in a reduction in the tear resistance of the modified materials relative to that of the unmodified material. The differences in measured parameter are more significant when the fabrics are tested along the weft and when TDFH is deposited (approx. 60%). However, the surface modification with HMDSO also results in a similar decrease in the measured properties by approx. 53% (Figure 2).

Moreover, observations of the tearing after the test show that the detected effect is the result of looser yarns instead of torn ones. The macroscopic imaging of the tearing area confirms the absence of torn yarns (Figure 3). The increased looseness of the woven structure is a direct result of the plasma modification process.

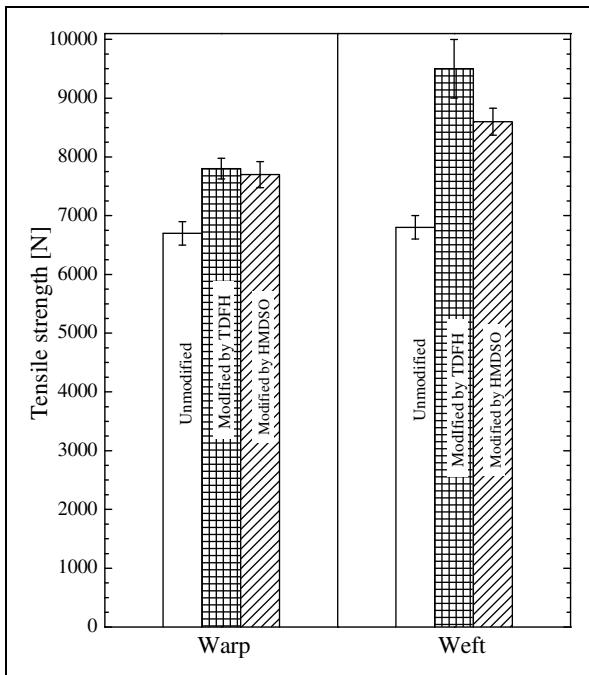
The loosening of the p-aramid woven fabric structure after the PACVD modification might affect



**Figure 2.** Tear resistance of the unmodified Kevlar® woven fabric and Kevlar® modified with HMDSO or TDFH.



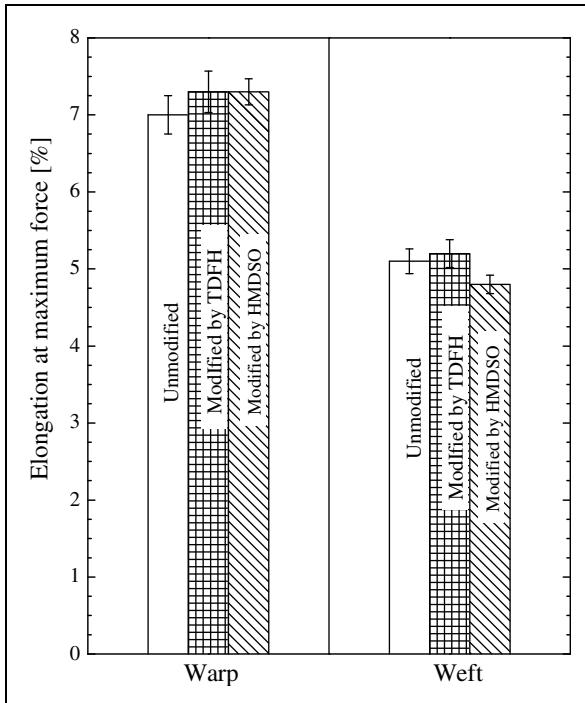
**Figure 3.** Kevlar® woven fabric modified with HMDSO by low-temperature plasma after the tear resistance test.



**Figure 4.** Tensile strength of the unmodified Kevlar® woven fabric and Kevlar® modified with HMDSO or TDFH.

the ballistic behavior of the designed soft inserts, and the effects of the surface modification on their behavior should be investigated in the next stage of the study.

**Tensile strength and elongation at the maximum force.** Both HMDSO and TDFH deposition lead to a significant increase in the tensile strength of the modified materials relative to that of the unmodified material (Figure 4). Similar to the tear resistance results, the differences are more significant when the tests are performed along the

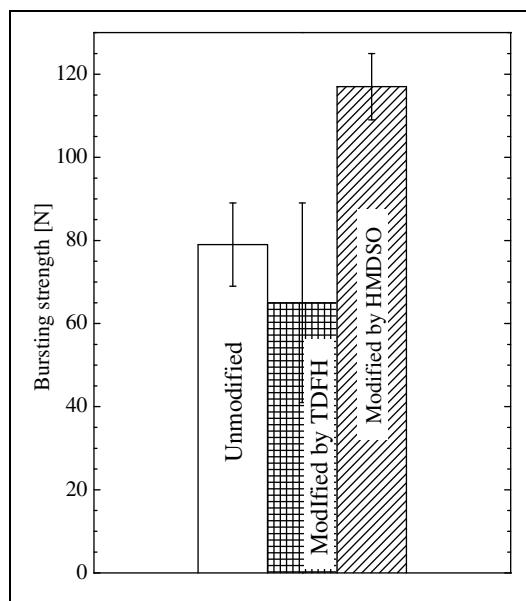


**Figure 5.** Elongation at the maximum force of the unmodified Kevlar® woven fabric and Kevlar® modified with HMDSO and TDFH.

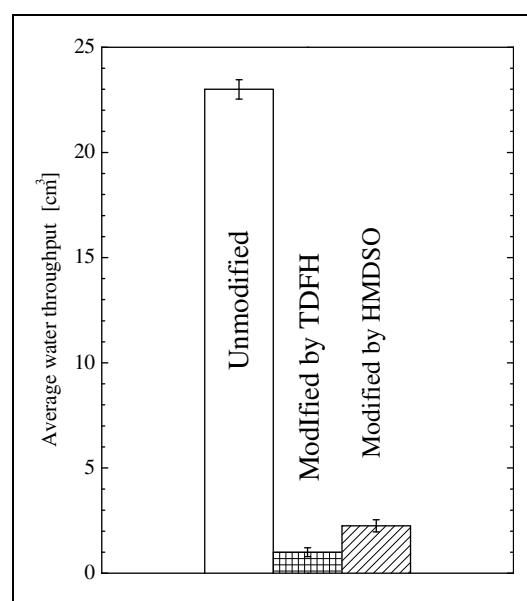
weft of the fabric. In contrast to the tear resistance results, the tensile strength increases when TDFH is deposited. Specifically, the low-temperature plasma treatment with TDFH leads to an increase of approx. 40% in the tensile strength, while the modification with HMDSO results in an increase of approx. 26%. The elongation results depend on both the stretching force direction and deposited compound. When the force is applied along the warp of the fabric, the effects of both the HMDSO and TDFH modifications are the same, i.e. the elongation parameter increases slightly (by approx. 4%) (Figure 5).

When the stretching force acts along the weft of the fabric, the modification with TDFH leads to a slight increase in the elongation (by approx. 2%), while the elongation decreases by approx. 6% when the surface is modified with HMDSO.

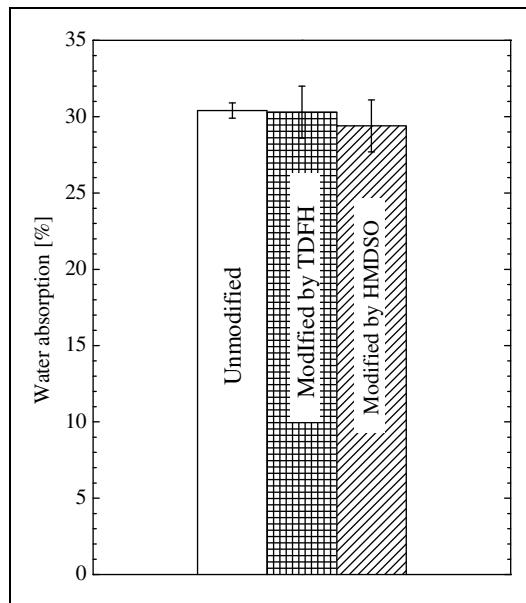
**Bursting strength.** The bursting strength results clearly show that one of the deposited compounds strengthens the fabric whereas the other weakens it. As shown in Figure 6, the HMDSO deposition causes a significant increase in the bursting strength (by approx. 50%), whereas the application of TDFH causes a decrease of approx. 20% in the bursting strength. The changes in the bursting strength are significant relative to the bursting strength of the initial raw material, indicating that the relatively short low-temperature plasma



**Figure 6.** Bursting strength of the unmodified Kevlar® woven fabric and Kevlar® modified with HMDSO and TDFH.



**Figure 8.** Average water throughput of the unmodified Kevlar® woven fabric and Kevlar® modified with HMDSO and TDFH.



**Figure 7.** Water absorption of the unmodified Kevlar® woven fabric and Kevlar® modified with HMDSO and TDFH.

treatment significantly alters the mechanical properties of the p-aramid woven fabric.

**Water repellence.** The wetting resistance of the fabric was studied by measuring the average water permeability and wettability. The results show that both TDFH and HMDSO deposition have little effect on its wettability as shown in Figure 7.

**Table 2.** Surface wetting resistance of the unmodified Kevlar® woven fabric and Kevlar® modified with HMDSO and TDFH

Low-temperature plasma treatment in the presence of:		
Initial materials	HMDSO	TDFH
I; I; I	3; 2; 2	4; 4; 3

I—the lowest resistance to wettability; 5—the highest resistance to wettability.

On the other hand, the low-temperature plasma treatment in the presence of HMDSO or TDFH has a positive effect on the average water absorption, i.e. both compounds significantly reduce the water absorption. The Kevlar® woven fabrics modified with TDFH and HMDSO showed significant decrease of the water throughput as compared to the unmodified fabric (Figure 8). This observation suggests that if the modified materials are used in the final ballistic panels, the resistance of the fabric to water penetration during standard use will be enhanced.

**Resistance to surface wetting.** As shown in Table 2, the low-temperature plasma treatment with TDFH or HMDSO increases the surface wetting resistance.

The low-temperature plasma treatment with TDFH results in a significant reduction in the wettability of the modified surface of the p-aramid woven fabric. The increases in the tested parameters are lower when the woven fabric is modified with HMDSO.

The low-temperature plasma treatment also reduces the water throughput of the materials considerably.

### **Modification of the Dyneema® composite**

**Tear resistance.** The initial sample and composites after modification via the low-temperature plasma treatment exhibit no tearing at the test conditions (acc. PN-EN ISO 4674-1:2005 Standard) as shown in Figure 9.

Due to the complex, compacted structure of the Dyneema® composite, no structure loosening is observed, unlike the results for both the unmodified and modified Kevlar® fabrics. The low-temperature plasma treatment does not lead to changes in the tear resistance of the UHMWPE composite, which is one of the main parameters affecting its ballistic performance.

**Tensile strength and elongation at the maximum force.** The deposition of TDFH increases the tensile strength of the modified material relative to that of the unmodified material.

However, the modification with HMDSO leads to a reduction in the tensile strength. This phenomenon occurs along both the longitudinal and vertical directions, but the impact of the surface modification is most clearly observed along the longitudinal direction, where the tensile strength changes by approx. 8% (TDFH) and 22% (HMDSO) (Figure 10).

The elongation at the maximum force depends on both the stretching force direction and type of deposited compound. The deposition of TDFH reduces the elongation in both the longitudinal and vertical directions. However, the decrease in the elongation is most clearly observed in the vertical direction (by approx. 17%).

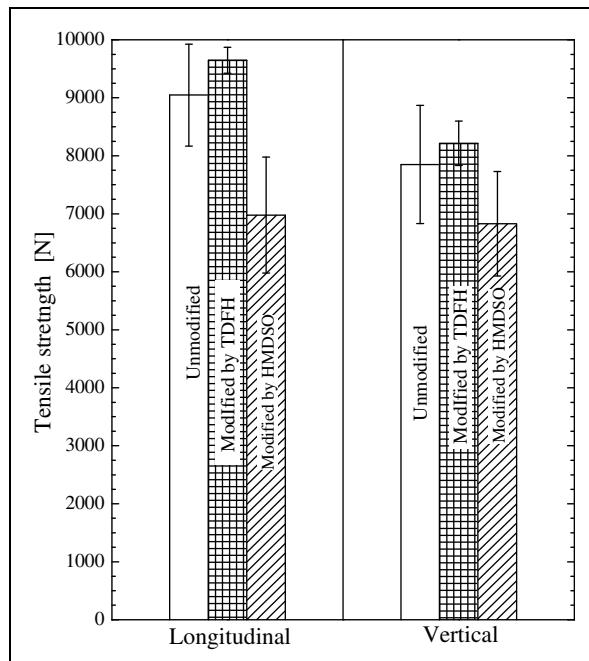


**Figure 9.** Dyneema® composite modified with TDFH by low-temperature plasma after the tear resistance test.

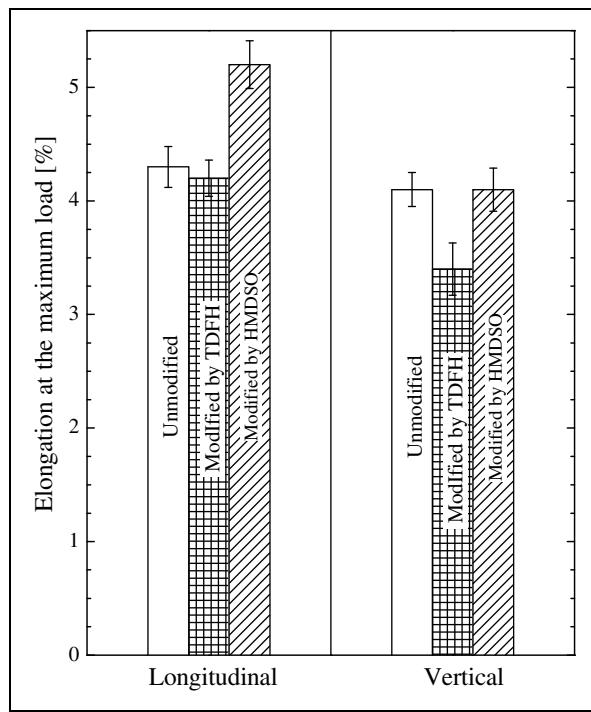
On the other hand, the modification with HMDSO results in a significant increase in the elongation along the longitudinal direction (by approx. 17%), while no change in the elongation is observed when the measurement is performed in the vertical direction (Figure 11).

**Bursting strength.** The bursting strength results clearly show that the modification with both deposited compounds leads to a slight weakening of the composite. As shown in Figure 12, the HMDSO deposition results in a slight reduction in the bursting strength (average by approx. 15%). However, due to statistical deviations, the bursting strengths of the unmodified composite and composite modified with HMDSO are comparable. The modification with TDFH results in amore significant decrease in the studied parameter (by approx. 66%).

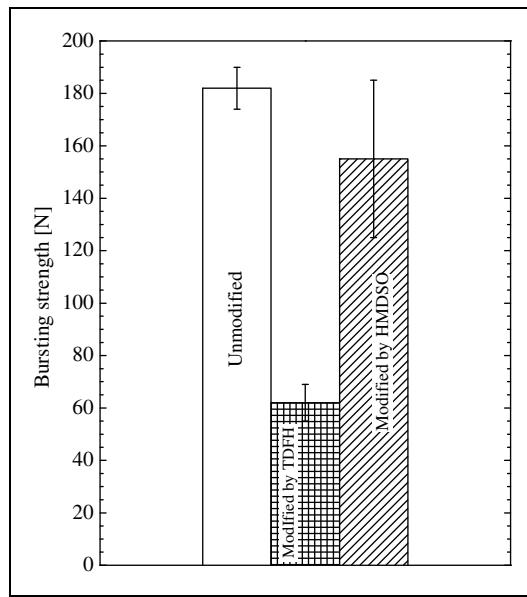
**Water repellence.** The water resistance results show that both TDFH and HMDSO deposition (especially TDFH) affected slightly on the water repellence of the composite (Figure 13). The increase in the average water absorption value was increase for TDFH modified materials by approx. 40%, whereas the modification using HMDSO yielded in increase by approx. 20% as compared with the raw materials. Above phenomenon can be explained by the increase in the surface enhance of the modified materials influencing slight



**Figure 10.** Tensile strength of the unmodified Dyneema® SB51 composite and Dyneema® SB51 composites modified with HMDSO and TDFH.



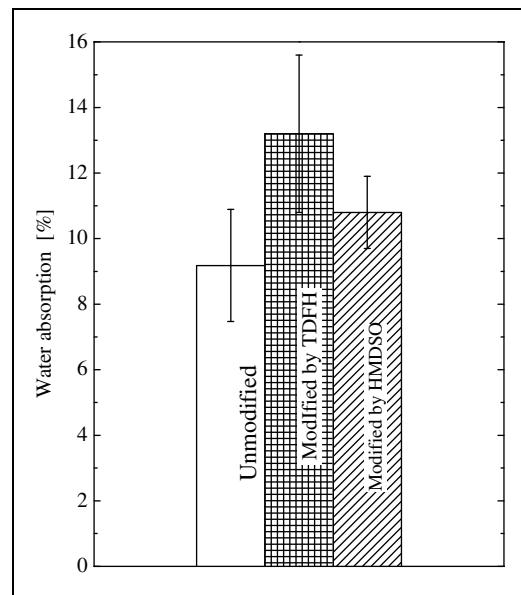
**Figure 11.** Elongation at the maximum load of the unmodified Dyneema® SB51 composite and Dyneema® SB51 composites modified with HMDSO and TDFH.



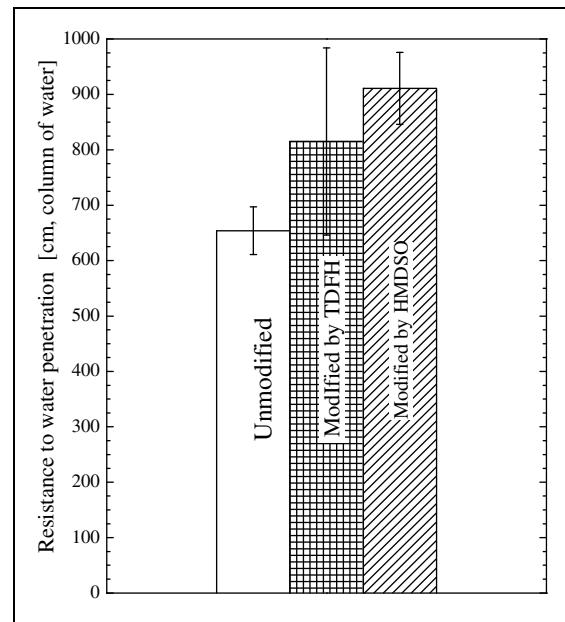
**Figure 12.** Bursting strength of the unmodified Dyneema® SB51 composite and Dyneema® SB51 composites modified with HMDSO and TDFH.

increase in the water particles capturing onto the composite surface.

Moreover, both modifications impact the resistance of the tested materials to water penetration. The TDFH



**Figure 13.** Water absorption of the unmodified Dyneema® SB51 composite and Dyneema® SB51 composites modified with HMDSO and TDFH.



**Figure 14.** Resistance to water penetration of the unmodified Dyneema® SB51 composite and Dyneema® SB51 composites modified with HMDSO and TDFH.

deposition leads to an increase of approx. 25% in the tested parameter, while the modification with HMDSO results in an increase of approx. 39% (Figure 14).

**Resistance to surface wetting.** The surface modification with TDFH or HMDSO during the low-temperature plasma treatment results in an increase in the surface

**Table 3.** Surface wetting resistance of the unmodified Dyneema® SB51 composite and composites modified with HMDSO and TDFH

Initial materials	Low-temperature plasma treatment in the presence of:	
	HMDSO	TDFH
3; 3; 3	4; 4; 4	4; 4; 4

1—the lowest resistance to wettability; 5—the highest resistance to wettability.

wetting resistance of Dyneema® SB51 in both cases (Table 3).

The observed changes in the surface wettability relative to that of the unmodified Dyneema® SB51 are smaller than those observed for the modified p-aramid woven fabrics. Moreover, the volume of water absorbed by the modified UHMWPE composites is similar to that absorbed by the TDFH-modified p-aramid woven fabric and lower as compared with HMDSO modified p-aramid woven fabric (Table 2).

## Conclusions

The effects of the PACVD modification of ballistic raw materials on their mechanical strength and water resistance were investigated. The results show that the appropriate choice of the deposited compound and selection of the process conditions can significantly change the surface properties of the initial (unmodified) material. A deposited thin layer of an organic compound increases the minimal stretching force required to mechanically damage the material. This layer can also transform the percolating textile into a nearly waterproof one. However, some of the mechanical strength parameters tested are not sensitive to the surface modification or are negatively impacted by it.

Until now, research has focused only on the modification of simple systems—single aramid fibers or UHMWPE fibers.<sup>1–8,10</sup> This work assumes that the fibers undergo a simple modification (as a preliminary attempt to assess the impact of modifying complex systems, namely UHMWPE fibers in a polymer matrix (Dyneema®) and raw aramid fabrics that were not initially purified). During the PACVD process, the initial purification stage used to prepare the surface significantly influences the main polymer layer deposition process. Including the purification process in the modification procedure shortens the overall process and makes it economically feasible.

The low-temperature plasma treatment leads to either a slight decrease or no change in the mechanical strength of the ballistic materials. UHMWPE

composite materials (i.e. Dyneema® or Spectra®) are relatively sensitive to high temperatures, especially those above their melting temperatures. The tensile strengths of Kevlar fabrics modified with fluorine- or silicon-containing organic compounds are greater than that of the unmodified Kevlar. In contrast, the tensile strengths and bursting strengths of the modified Dyneema® composites, especially the composite modified with the silicon-containing compound, are smaller than those of the unmodified composite. These results emphasize the greater sensitivity of the UHMWPE matrix to the modification process conditions. The effect of the decrease in the mechanical strength of the modified UHMWPE composite on the ballistic performance will be studied to determine the correlation between the mechanical and ballistic behaviors of the modified materials.

The results indicate that the use of PACVD to deposit a polymer layer on the fiber (Kevlar®) and UHMWPE composite (Dyneema®) surfaces might significantly improve the important material properties:

1. Water resistance of the p-aramid fibers is improved (degradation from water exposure is a main factor leading to a loss in the fiber strength, which eventually weakens the ballistic behavior). Consequently, the ballistic protections can be used for a longer period of time without a significant loss of product performance and safety.
2. The surface properties of both studied ballistic materials can be changed in a controlled way, which is helpful for, e.g., the fabrication of a hybrid composite consisting of more than one type of ballistic or non-ballistic material. The combination of materials with different performances might significantly improve the main functionality of the fabricated composites and provide them with new functionalities.

Moreover, the outcomes of this work show that PACVD is promising for ergonomics studies and the transformation of textiles such as Kevlar® and Dyneema® into materials used for protection against firearms.

The results presented here are initial tests, and terminal ballistic tests will be performed in the near future. In the next stage of this research, the effects of the PACVD modification on the ballistic behavior (resistance to fragments and bullets acc. the PN-V-87000 Standard for a soft ballistic system optimized for the K2 bullet-proof class and O2 fragment-proof class) and stability of the modification effects during accelerated aging studies (aging factors: temperature, humidity, UV light) will be studied. Moreover, the PACVD modification of the ballistic raw materials with HMDSO and

TDFH will be described using ATR-FTIR spectroscopy, DSC and SEM-EDS. The topography of the modified fibrous materials will also be studied using SEM microscopy.

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