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Review

Composites in Ballistic Applications Focused on Ballistic Vests—A Review

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Abstract: The development of ballistic materials has improved very rapidly in the last few years. Body armor plays an important role in protecting individuals during military threats. Body armor can be divided into hard and soft variants depending on the trade-offs between protection levels and wearer agility. Current research aims to optimize strength-to-weight ratios by using different combinations of synthetic or natural fibers or their combinations to achieve increasingly demanding requirements for ballistic materials. Moreover, it examines the various types of fibers utilized in the construction of body armor, ranging from traditional materials like metal and ceramic to synthetic and natural fibers. This paper discusses ongoing research efforts aimed at further enhancing the performance of these materials, such as the incorporation of modified natural fibers into advanced composite systems. The review provides a comprehensive analysis of the current state of the materials utilized in ballistic protection.

Keywords: composite materials; ballistics; natural fibers; nanomaterials

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1. Introduction

Body armor is used to protect people, mainly during military riots and terrorist attacks. In the past, traditional body armor, including vests, was heavy and uncomfortable to wear, and it also affected the mobility of soldiers. Contemporary body armor includes ballistic vests, helmets, leg or groin protection, and even specific plates used to provide additional protection. Ballistic vests are an important part of body armor because worldwide conflicts and violence are currently on the rise [1–8].

Body armor can be mainly classified into two categories, hard body armor and soft body armor. Hard body armor guarantees protection levels III and IV, according to the National Institute of Justice (NIJ). It is mainly reinforced with metal, ceramic, or fiber-based composite plates within layers of fabric. This type of body armor protects against high-speed bullets or projectiles fired from ranged weapons and it is used especially by military personnel in high-risk operations. Its disadvantage is heaviness and rigidity; thus, it restricts the wearer's movement [6,9,10].

On the other hand, soft body armor is primarily made of multiple layers of high-performance fabrics. These types of fabrics make this type of body armor lighter and more flexible than materials such as metal or ceramic used in hard body armor. Soft body armor has lower protection levels—II-A, II, and III-A (according to the NIJ), and it is mainly used by the police, security personnel, riot officers, etc. However, soft body armor is heavy enough to restrict the wearer's agility. Nowadays, these limitations bring several challenges when it comes to the reduction in weight and improvement in the efficiency of handling multiple ballistic shots. Simultaneously, in terms of movement and comfort, flexibility is also a very important part when it comes to body armor [11–16].

Body armor materials have a long history that dates to the beginning of human civilization. Already in the medieval ages, the Japanese developed a soft body armor made from silk. At the end of the 19th and the beginning of the 20th century, the US military considered the possibility of using soft body armor made of silk. However, it was found that such armor is only effective against low-velocity projectiles (up to approx. 120 m/s) and did not offer protection against newly introduced types of ammunition back then, which reached the speed of approx. 180 m/s. During the Second World War, so-called "flak jackets" were developed, which were light armor that did not offer enough protection against direct fire from a rifle or machine gun but were designed to protect against flying debris and shell fragments. The first flak jackets contained manganese steel plates, the latter generation of flak jackets replaced manganese steel with other materials, such as nylon or fiberglass plates. In the 1960s, high-performance para-aramid fibers (Kevlar®) by DuPont were invented and eventually used in soft body armor. This type of fiber protects against bullets, hand grenades, and knife attacks. Nowadays, high-performance fibers, including para-aramid (Kevlar®, Technora®, Twaron®), poly p-phenylene benzo-isoxazole—PBO (Zylon®), ultra-high-molecular-weight polyethylene—UHMWPE (Dyneema®, Spectra®), or composites with natural fibers, are used in body armor [14].

Currently, researchers are looking for ways to develop a ballistic material with the highest strength and minimum weight. The mentioned properties are essential because the wearers of body armor are often on the move, and lightweight body armor ensures better movement capabilities. Another essential property of body armor is good energy-absorption capability; for the improvement thereof, shear-thickening fluid was tested. The new generation of ballistic vests also tends to have several advanced features that can monitor the wearer's life condition in harsh environments. These features can be used for health monitoring like heart rate or body temperature [17–24].

This review is focused on the current development of the fibers used in ballistic protection, mainly aimed at fibers (especially natural and synthetic) or composite materials in ballistic vests. The main goal of this review article is to focus on a clear and comprehensive treatment of the current state of materials suitable for ballistic protective elements, such as a ballistic vest. It is important to review what mechanical properties each material has. Even the excellent properties of currently used synthetic fibers such as Kevlar and Spectra or composite systems may not be able to fulfill the increasingly sophisticated requirements for anti-impact performance relative to the weight or volume of the material used. Using modified natural fibers in high-tech ballistic composite systems is becoming increasingly important, and the usage thereof is gaining growing attention from research organizations dealing with ballistic protection of the human body.

2. Natural Fibers in Body Armor

Natural fibers have become an ecological and economical alternative to existing composites not only in ballistic applications. The aforementioned natural fibers come from various materials, including plants, animals, and other resources. Plant-based fibers are obtained from various types of vegetation, such as leaf stems (e.g., bagasse, ramie, banana, abaca, bamboo, pineapple), fruits (e.g., cotton and coir fibers), bast (e.g., flax, hemp, kenaf, jute), grass (e.g., bamboo, Indiangrass, switchgrass), straw (e.g., corn, rice), or wood pulp. The samples of plant-based fibers are shown in Figure 1. Animal-based fibers, such as avian fiber, goat hair, horsehair, and wool, consist of bones, shells, feathers, and furs. These biological fibers must be biodegradable and non-harmful to the human body when they meet human skin. Natural fibers used for nowadays ballistic and bulletproof applications are mainly sisal, curaua, mallow fibers and coir, ramie, jute, giant bamboo, wool, and sugarcane bagasse waste [25–28].

Natural fibers, in common, have many favorable properties and are an attractive alternative to synthetic fibers because of their low cost, lightweight, minimal health hazards during processing, biodegradability, reasonably good specific strength and elastic modulus, good thermal and acoustic insulation characteristics, ease of availability, etc. However, in their raw state, they have high water/moisture absorption or may contain dead cells, wax, and oil. The higher moisture absorption of these fibers causes their lower mechanical properties. Therefore, it is necessary to modify the fiber´s surface. Methods include adding coupling agents, chemical treatment, enzymatic treatment, and corona/plasma treatment. This improves the connection between the matrix (polymer) and the reinforcement (natural fiber), which increases the strength of the composite fabricated. To achieve a reduction in moisture content, a low cellulose content is needed, thus resulting in a weakening of the bonds between adjacent fibers and enhanced interfacial adhesion between parts. The modifications of natural fibers improve their overall applicability for high-end ballistic applications [29–38].

Figure 1. Samples of plant-based fibers.

Table 1 presents the physical properties of various natural fibers commonly used in textile and composite applications. The properties included are elongation at break (%), tensile strength (MPa), tensile elastic modulus (GPa), density (g/cm^3), moisture content (%), and diameter (µm). These properties are crucial in assessing the suitability of each fiber for specific applications, including ballistic protection. Several materials have a great property for ballistic vests. The nettle fiber has exceptional tensile strength and high tensile elastic modulus. Sisal fiber offers a good balance of strength and weight for ballistic protection. Spider silk possesses remarkable tensile strength and elasticity, which make this fiber a promising candidate for enhancing the durability and flexibility of ballistic vests while maintaining lightweight protection. Due to the relatively low density, nettle fiber, ramie fiber, coconut fiber, and sisal are lightweight, which makes this fiber suitable for ballistic vests.

Table 1. Physical properties of selected natural fibers [24,25,39–50].

Fiber		Elongation at Break (%)	Tensile Strength (MPa)	Tensile Modulus (Gpa)	Density (g/cm^3)	Moisture (%)	Diameter (µm)
Bast	Flax	1.2–1.6	345–1035	28–80	1.2–1.5	8–12	12–20
	Hemp	1.0–4.0	300–700	20–70	1.3–1.5	6.2–12.0	25–600
	Nettle	2.3–2.6	1594	87	0.72	-	19–47
	Jute	1.3–3.0	350–780	20–30	1.3–1.5	12.6–13.7	25–250
	Kenaf	2.7–6.9	150–250	10–20	1.1–1.2	9.0–12.0	30–40
Leaf	Sisal	2.0–14.0	350–840	9.0–38	0.7–1.5	10–22	50–200
	Abaca	2.0–14.0	350–840	9.0–38	0.7–1.5	10–22	50–200
	Henequen	3.00–4.7	4.30–5.8	0.7–2	1.1–1.4	25	25
	Palm	0.8–14.5	148.4	10.5	0.8–1.6	14.0	50
	Banana	1.0–9.0	54–914	7.7–32.0	0.7–1.4	8–10	100–250
	Ramie	2.5–3.8	400–560	1.24–5	1.5–1.5	12	25–30
	Date Palm	3–17	300	2–12	0.6	25	19–29

Table 1. *Cont.*

Fiber		Elongation at Break (%)	Tensile Strength (MPa)	Tensile Modulus (Gpa)	Density (g/cm^3)	Moisture (%)	Diameter (µm)
Fruit/Seed	Coconut	15–21	140–225	3–5	1.2	15	50–300
	Oil palm	3.6	30	1–5.7	0.9	9.3	150–700
	Sponge gourd	-	140	28	0.71	11	75–200
	Kapok	1.8–4.2	45–64	1.7–1.6	0.29	8.5	20
	Cotton	7.9	410	5–13	1.5	6.5–8	8–20
Grasses	Straw-wheat	18	21–31	1.4	0.2	10	5.7
	Straw-rice	2.3	30	2.6	0.3–0.4	15–18	250
	Straw-rye	2.5–5	16–33	250	0.56	17–18	20–30
	Bamboo	1.3–7.0	140–800	11–35	0.6–1.1	11–17	88–125
Husk/Hull	Rice husk	8	14–54	0.3–2.9	0.9–1.5	10–15	14
Sugar	Sugarcane bagasse	0.9–3.8	20–350	0.5–27.1	0.6–1.3	45–55	10–25
Minerals	Basalt	3.15	2.8–3.1	89	2.8–3	5–15	10–20
Animal	Spider silk	30	2000	30	1.3	-	3
	Wool	35–45	1–1.7	2.3–3.4	1.3	16–18	10–24

3. Synthetic Fibers in Body Armor

Standard materials, such as ceramic or steel, have recently been replaced by synthetic fiber materials. Synthetic fibers are the optimal choice for lightweight and flexible body armor because they can be high strength, flexible, stretchy, rigid, and have a water absorbency according to requirements. Most of these materials are also characterized by high-temperature stability and strength-to-weight ratio. Lightweight ballistic vests are constructed primarily from Kevlar, Aramid, Twaron, Ultra-High-Molecular-Weight Polyethylene (UHMWPE), or nylon fibers because those fibers provide high elastic modulus and impact strength [21,47].

The main advantage of synthetic fibers is their increased resistance to water, stains, heat, and chemical damage, compared to natural fibers. Synthetic fibers are also more resistant to chemical decomposition because they are not susceptible to biodegradability, and they cannot be disrupted by various bacteria and fungi [51]. The chemical properties of these fibers and fabrics can be converted or modified to obtain the needed features for the manufacturer [52].

The disadvantage of synthetic fibers is that they are not easily degradable, which makes them an ecological burden [53]. Other disadvantages of some synthetic fibers, such as polypropylene, polyester, or nylon, are lower melting points and chemical composition. Some of these fibers are more sensitive to heat damage when washed in hot water, and they may also have an increased tendency to generate electrostatic charges [54]. However, the main disadvantages of synthetic materials are that they can be harmful to human skin and can cause allergic reactions. Moreover, some of these fibers, such as polyester and nylon, cannot drain perspiration as efficiently or quickly as natural fibers. That is why these fibers are combined with natural fibers (cotton or wool) to achieve required properties like strength and elasticity, wrinkle, and tear resistance [55,56].

Apart from properties such as the type or performance of the fibers used, the most important feature of ballistic protection depends on the nature of the yarn, the fabric construction, the number of layers, and the type of layers used in the structure [57–60].

Synthetic fibers have a wide range of properties, especially in terms of their elasticity modulus, which is a crucial characteristic when using fibers to create composite materials. The macroscopically symmetrical, elastic material known as synthetic fiber has a low cross-section and a high length-to-thickness ratio. The chemical and physical properties of synthetic fibers are determined by the structure of a polymer matrix in a three-dimensional space. When it comes to synthetic fibers, the preferred configuration is achieved by using mechanical drawing operations, where the fiber is stretched out to multiple times its original length shortly after extrusion. This produces the preferred orientation [51,53]. The most popular methods for producing synthetic fibers are melting, drying, and wet spinning (Figure 2) [56,61,62].

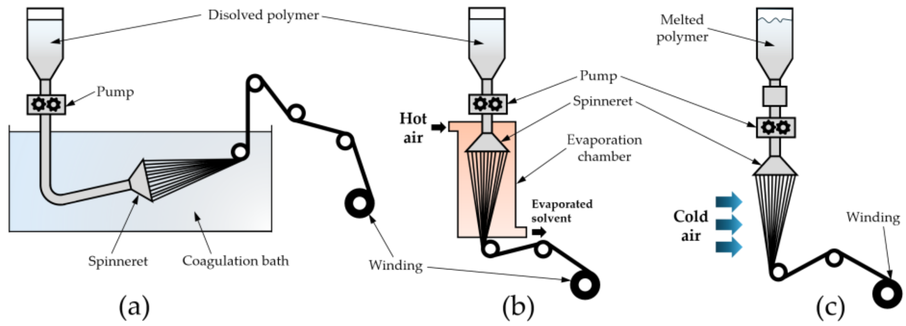

Figure 2. Diagram of (**a**) wet spinning, (**b**) dry spinning, and (**c**) melt spinning.

High-performance synthetic (polymer-based) fibers include para-aramids (Kevlar and Twaron), Ultra-High-Molecular-Weight Polyethylene–UHMWPE (Spectra, Dyneema, Technora), and liquid-crystal polymer fibers (Zylon and Vectran). Polymeric materials are used in ballistic applications because of their lightweight, and high strength. On the other hand, they also may be vulnerable to high temperature, UV light, radiation, humidity, etc. The main properties of aramid fibers are lightweight, high strength, elastic modulus, good impact strength, wear-, chemical-, heat- and corrosion-resistance, cut-, puncture-, and flame-retardation, hybrid tailoring, and blending ability, fatigue and creep balance, dimensional stability, and high energy dissipation. Aramid fiber is not only used for ballistic vests but also for military helmets, fireproof clothing, walking boots, diving, gloves, cut-resistant gloves, tires, etc. In contrast to ceramic, carbon, glass fibers, and aramid fibers can be easily woven into textile looms. Another category of polymer-based high-performance fibers is UHMWPE fibers, which can be used in ballistic applications as woven fabrics and composites. The difference between woven fabrics and composites is that woven fabrics have lower ballistic performance due to their low coefficient of friction. When manufactured with the gel-spun UHMWPE technology, those fibers are lighter than water, and ropes made of such material float. UHMWPE gel-spun fibers made by Spectra are ten times stronger than steel, but the melting temperature is low with a tendency to creep at high loads. Usage of UHMWPE has a wide range of applications such as ballistic vests, helmets, shields, vehicle protection, etc. Liquid-crystal polymer fiber is a sub-category of thermoplastic polymers prepared by melting and spinning the crystal polymer at high temperatures [63–66].

Para-aramid, exemplified by Kevlar 129, has an impressive combination of high tensile strength, substantial tensile elastic modulus, and moderate density. This makes this material an excellent choice for ballistic vests requiring top-tier protection without sacrificing flexibility. Similar to para-aramid, UHMWPE, specifically Spectra 2000, offers re-markable tensile strength and an outstanding tensile elastic modulus at a remarkably low density. This combination makes Spectra 2000 ideal for crafting lightweight and robust ballistic protection. Liquid-crystal polymer, represented by Vectran, is a great material for ballistic vests requiring durability and flexibility. In conclusion, these fibers stand out for their exceptional performance attributes, offering promising solutions for the development of next-generation ballistic vests. The following Table 2 lists the physical properties of selected synthetic fibers.

Shi et al. [64] tested the impact resistance of 3D woven composites with hexagonal binding patterns. Composite specimens made of para-aramid/polyurethane, 3D woven with three kinds of fiber volume fractions, were prepared by compression resin transfer molding. The research [34] found that the fiber and resin damage area of the impact surface was about 1.5 to 3 times bigger than the area of the projectile. Based on the results, this study proved that 3D woven composites of para-aramid/polyurethane are suitable for ballistic applications. Another study conducted by Chu and Chen [65] also focused on para-aramid, namely, Kevlar, with different weave architectures. This study showed that plain weave fabric has the highest energy absorption compared to twill and basket weaves, especially for the low-velocity impact. It also proved that the tested Kevlar did not have enough strength to stop 9 mm Parabellum projectiles. Similar research conducted by Stopforth and Adali [66] further investigated the Kevlar for body armor using 9 mm projectiles to determine the weight and number of layers of Kevlar and ballistic gel required to stop the projectile.

Table 2. Physical properties of selected synthetic fibers [28,49,50,63,67–72].

Fiber Type		Fiber	Density (g/cm^3)	Tensile Strength (GPa)	Tensile Modulus (GPa)
Nylon	Nylon 6	1.14	0.5	3	18–26
Para-aramid	Technora, Teijin	1.39	3	70	4.40
	Twaron, Teijin	1.45	3.10	121	2
	Kevlar 29	1.44	2.97	70	4.20
	Kevlar 129	1.44	3.39	96	3.50
	Kevlar 49	1.44	2.97	113	2.60
	Kevlar KM2	1.44	3.30	70	4
UHMWPE	Spectra 900	0.97	2.40	73	2.80
	Spectra 1000	0.97	2.83	103	2.80
	Spectra 2000	0.97	3.34	124	3
	Dyneema	0.97	2.60	87	3.50
Liquid-crystal polymer	Vectran	1.47	3.20	91	3

4. Mineral and Carbon-Based Materials

The term mineral materials refers to ceramic materials and glass fibers. Ceramic materials are divided into two categories, oxide ceramics (alumina ceramics with various contents of Al_2O_3) and non-oxide ceramics (nitrides, carbides, borides, or their combination). Alumina is mostly used as ceramic material in ballistic applications due to its high density, physical properties, low cost, and easy production. Other types of non-oxide ceramics materials, such as silicon carbide (SiC), boron carbide (B_4C), silicon nitride (SiN), and titanium diboride (TiB_2), are more expensive compared to alumina [73–77]. Moreover, ceramic materials and their composites are lightweight materials that can provide a level of armor protection comparable to high-hardened steel. Another advantage of ceramic materials is their high strength and high-elastic modulus properties. These materials also have disadvantages, such as brittleness and sensitivity to cracking due to rapid temperature changes. However, the advantages of these materials often outweigh their disadvantages, and they are often used in hard ballistics. The cost of these safety features is relatively high, in comparison to equally or better performing but cheaper, lighter, more flexible materials that are able to wick sweat away from the human body [73,74,77,78].

Another group of mineral materials is glass fibers, which are characterized by an outstanding strength-to-weight ratio and flexibility; thus, enabling the manufacture of lightweight yet highly resilient ballistic material that contours the wearer´s body. All these features contribute to the wearer´s comfort and mobility in demanding situations. Glass fibers are also impact-resistant and suitable for absorbing and dispersing the impact of projectiles, which significantly contributes to the vests´ effectiveness in reducing ballistic trauma. Finally, glass fibers are cost-effective and readily available, making the ballistic gear affordable protective equipment for people working in high-risk areas. The disadvantages of glass fibers include their sensibility to moisture and certain chemicals, which can damage their structural integrity over time. The impact resistance and strength of glass fibers are limited in comparison to some other high-performance fibers, such as para-aramid or ultra-high-molecular-weight polyethylene. Glass fibers are, in comparison to the aforementioned high-tech materials, generally more brittle, which negatively affects their ability to withstand repeated impacts. These characteristics require proper handling and maintenance of glass fiber ballistic gear to keep their long-term durability and efficiency while providing reliable protection [29,63,71].

Carbon-based fibers are a superb option for ballistic vests because they offer excellent protection against most projectiles and yet are lightweight and flexible, thus enhancing the comfort and agility of the user. Carbon fibers are characterized by exceptional strength-to-weight ratio, high tensile strength, and impact resistance. Ballistic gear made of carbon fibers is rather durable enabling their long-term use without affecting their defensive capabilities. The primary disadvantage of carbon fibers is their high price, which makes them relatively expensive to manufacture and, in certain ways, limits their widespread affordability. Like glass fibers, carbon fibers are sensitive to damage from high-velocity impacts due to their brittleness. In addition, carbon fibers are vulnerable to damage from certain chemicals, requiring caution in their storage and handling to maintain their long-term usability and effective protection in ballistic applications [76–78].

Glass fibers, particularly S-Glass, offer high tensile strength, elastic modulus, and strain-to-failure ratios, making them suitable for ballistic vests. Silicon carbide ceramic fibers excel in strength and elastic modulus, ideal for extreme impact resilience. Carbon fibers like Celion provide a lightweight strong option, ensuring comfort and protection in ballistic applications. The following Table 3 presents the most-used types of mineral and carbon fibers in ballistic vests.

Table 3. Physical properties of mineral and carbon fibers [49,79–87].

Fiber Type		Density (g/cm^3)	Tensile Strength (GPa)	Tensile Modulus (GPa)	Strain to Failure (%)
Glass	S-Glass	2.48	4.40	90	5.70
	E-Glass	2.63	3.50	68.50	4
Ceramic Fibers	Alumina	250	1.72	152	2
	Silicon Carbide	280	4	420	0.60
Carbon Fiber	Standard	1.75–2	3.65	33.50	1.50
	Celion	1.80	4	230	1.80
	Aksaca	1.78	4.20	240	1.80

5. Composite Materials in Ballistic Vests

Composites consist of different materials that have different chemical or physical properties. Depending on what properties are required for the application, a specific composite is prepared. Composite materials are often divided into categories that are metal composites, ceramic composites, polymer composite materials, composites with natural fibers, or combinations. Aramid, carbon, and glass fiber composites are widely used in ballistic applications such as ballistic vests because of their excellent properties including low weight, toughness, and high tensile elastic modulus [88].

Polymer composites gained high demand due to their lightweight, high strength, and good mechanical properties, together with chemical and corrosion resistance. Apart from a great weight-to-strength ratio, these composites have other advantages like high rigidity and high design freedom. Therefore, the use of polymer composites is growing rapidly in many applications, such as ballistics, car interiors, airplanes, spacecraft, ships, civil construction, packaging, and sports equipment [26–28,30–32].

Polymer composites reinforced with synthetic or mineral materials are widely used and studied. The scientific community is returning to natural materials added to these composite systems. Natural fiber-reinforced polymer composites are often made by regular manufacturing methods used in thermoplastics and conventional fiber-reinforced polymer composites. These methods include compression molding, injection molding, extrusion, resin transfer molding, vacuum infusion, hand lay-up, and filament winding. The manufacturing technology can significantly affect the mechanical load resistance of the composite system. One way to further increase the impact resistance of the composite is by coating, which can provide high protection by absorbing high energy in a very thin layer [89,90].

In the last few years, materials such as natural latex, graphite oxide, shape memory alloys, and shear thickening fluid (STF) were explored to improve the ballistic performance of woven fabrics [61,90–92]. STF is non-toxic and has great thermal stability. It is a fluid or gel composed of highly concentrated small particles such as silica or calcium carbonate dispersed in hygroscopic liquid polymers like polyethylene, glycol, or ethanol. The viscosity of this fluid is based on the rapid response of its shear rate or shear stress. Studies have shown that the application of STF on fibers, such as Kevlar or UHMWPE, has increased their energy absorption capability compared to those without STF (Figure 3). By impregnating the fibers with STF, the friction between the yarns limits the tension on these yarns during impact [92–96]. It was also found that adding a small amount of silicone carbide, as a dispersant phase, into STF increases the stab resistance of STF-impregnated aramid fabric [70,90,93,97].

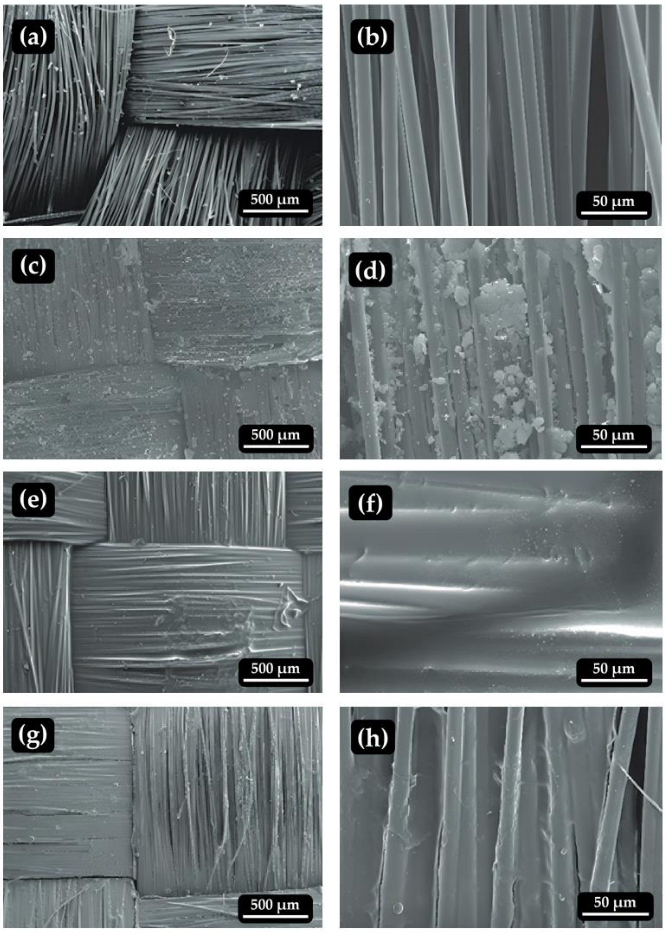

Figure 3. SEM images of the (**a**,**b**) Neat Kevlar plates; (**c**,**d**) STF/Kevlar plates; (**e**,**f**) Epoxy/Kevlar plates; (**g**,**h**) Polyurea Elastomers/Kevlar plates [97].

Rajole, Ravishankar, and Kulkarni [98] studied the ballistic performance of jute/rubber and glass/epoxy sandwiches. Energy absorption tests showed that the created sandwiches of jute/rubber and glass/epoxy can be used as low-cost protective materials for ballistic vests. The hybridization method of carbon/aramid fiber, conducted by Xu et al. [99], was used to improve the roughness of composite materials in ballistic applications. This method offers better features in terms of mechanical strength in comparison to non-hybrid composites. Another study, conducted by Dewapriya and Meguid [100], deals with the impact resistance of multilayer graphene/polyethylene composites. The results showed that the ballistic impact resistance of polyethylene covered by one layer of graphene membrane is increased by over eight times. Moreover, the multilayered graphene/polyethylene nanocomposites could potentially provide even better protection against hypervelocity impacts. Wu, Sikdar, and Bhat [101] studied the ballistic impact resistance of Twaron/graphene oxide twice-filtrated panels. It was found that these panels absorbed 50% more energy than the plain fabrics. Besides aramid itself, the grafting with graphene oxide increased the interfacial shear strength by 210%.

6. Nanomaterials in Ballistic Applications

Although nanomaterials and nanofibers are rarely used for the fabrication of ballistic materials, they can be used for merging with composites to create nanocomposites. These nanocomposites are used and studied as a bullet-resistance material [101,102]. The unit size of nanomaterials is approximately between 1 and 100 nm. Nanomaterials are grouped into several dimensions, which are 0D such as fullerenes; 1D such as carbon nanotubes (CNTs); 2D such as graphene nanoplatelets (GNPs); and 3D such as nano graphite [103].

The surface of carbon nanotubes is made from pentagonal and hexagonal patterns bonded with carbon atoms. This structure is a hollow cylindrical tube formed by rolling 2D graphene sheets [103]. This material is considered a 1D nanomaterial because the diameter of the tubes is in the nanoscale with a length of 1 mm. The main properties of carbon nanotubes (CNTs) are excellent mechanical strength and high thermal conductivity through carbon atom vibrations. It is one of the strongest nanomaterials with a tensile strength of up to 200 GPa, relatively low density, and modulus higher than 1 TPa [102,103]. Such advantages make this material favorable for creating high-performance nanocomposites. Ghosh and Ramajeyathilagam [104] tested a composite material made of multi-walled carbon nanotubes and alumina nanoparticles to determine the impact resistance of the merged material. The study found that the addition of nanofillers positively affected the material in terms of enhancing impact resistance.

Graphene as a 2D nanomaterial is constituted of a single layer of carbon atoms arranged in a hexagonal pattern with a carbon atom thickness of ~0.335 nm (Figure 4) [87,105]. Graphene possesses unique properties such as a high tensile strength of 130 GPa, and a high elastic modulus of 1 TPa. It also has exceptional electrical conductivity and good thermal conductivity [106]. Graphene has penetration energy around 10 times higher than microscopic steel sheets. Due to the mentioned properties, this nanomaterial is widely explored in nanocomposites for ballistic impact applications. Vignesh, Surendran, Sekar, and Rajeswari [107] studied the effect of ballistic impact on Kevlar-29 reinforced with graphene nanolayers. The ten layers of graphene nanosheets were inserted between the Kevlar-29 fiber layers. It was found that this approach significantly improves the ballistic resistance of the mentioned material [108–115].

Nanoclay is composed of mineral silicate layers that are stacked together by weak physical bonding. This material has a sheet structure and a high aspect ratio with a 1 nm thickness. It can be categorized into several groups such as hectorite, bentonite, kaolinite, montmorillonite, and halloysite. Nanoclay is often embedded into fiber-based polymer composites due to its anti-impact enhancement function and cost-efficiency, making it a great alternative to organic nanofillers for mechanical and ballistic performance enhancement [101,103,116].

Several authors [117–119] dealt with the impact resistance of composite materials with nanofillers. They found that adding nanofillers improves the impact resistance of the used material. Dass, Chauhan, and Gaur [117] tested the low-velocity impact behavior of nanofillers dispersed in epoxy resin of carbon fiber-reinforced polymer, offering better impact resistance. Kaybal, Ulus, Demir, Sahin, and Avci [119] tested the impact resistance of glass/epoxy laminates reinforced with nanoclay and graphene nanosheets. The impact resistance properties of the mentioned material were improved compared to the unreinforced material. It was found by Pol and Liaghat [120] that the glass fiber/epoxy/nanoclay composite may, due to adding the nanoclay, achieve a higher ballistic limit than the neat composite (42% higher). This material also reduces the average damaged area under ballistic impact. Moreover, added nanoclay can change mechanical performance and crack propagation velocity, which improves ballistic resistance. Fiber-based polymer composites like para-aramid, glass, or carbon fiber can influence the studied material. Another nanomaterial is tungsten disulfide, which has an inorganic structure similar to molybdenum disulfide. Tungsten disulfide has 2D stacked molecular sheets. Tungsten disulfide has high chemical stability, ultra-low friction, good elasticity, high stiffness, excellent compression resistance, and outstanding shock-absorbing ability. The properties and low cost make this material highly desirable and practical for ballistic impact applications. Tungsten disulfide and molybdenum disulfide have been studied as reinforcing fillers in ballistic protective and energy absorption materials [101,121].

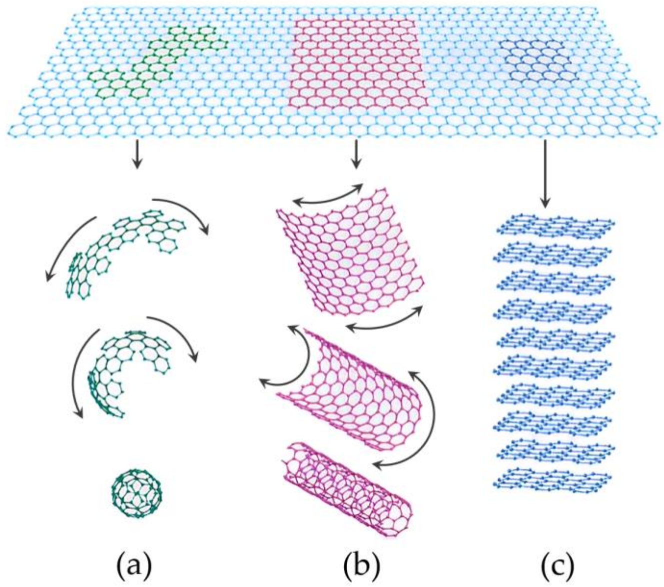

Figure 4. Graphene (**a**) wrapped up into 0D buckyballs, (**b**) rolled into 1D nanotubes, and (**c**) stacked into 3D graphite [115].

The potential of tungsten disulfide and inorganic nanotubes tungsten disulfide in ballistic applications was studied by several authors [121,122]. It was found that the usage of these nanomaterials, due to their low cost and many advantageous properties, such as chemical stability, ultra-low friction, good elasticity, high stiffness, excellent compression resistance, and outstanding shock-absorbing ability, makes this material suitable for ballistic applications. The conducted studies have shown that the nano-reinforced material displayed higher tensile strength, higher toughness, and lower deformation when compared to the material without nano-reinforcement [121,122]. Another study [123] deals with the modification of e-glass polyester composites with silane-functionalized alumina nanofibers. The results showed that this composite modification could increase the ballistic limit of the material.

The above-mentioned nanomaterials, such as carbon nanotubes, nanoclay, and graphene, are materials that are being intensively researched as high-performance ballistic impact materials. Other nanomaterials, such as boron carbide, core-shell rubber nanoparticles, halloysite nanotubes, and bucky paper, have also been incorporated into composites or STFs to improve their impact resistance, mechanical strength, and energy absorption capability.

Another group of nanomaterials is nanofibers, which are materials synthesized at a nanoscale of 100 nm or less for at least one dimension. They have one or more dimensions less than 1 μm, and the size of the nanofiber is around 0.1–1 μm. In comparison to conventional fibers, this material has smaller diameters, a lighter weight, highly porous structures, and much larger surface-to-volume ratios, which make it ideal for various applications. Nanofibers can also be added to composites for ballistic applications due to their chemical and physical properties, such as good mechanical, thermal, and energy absorption [67,86,101].

7. Future Developments

Future development of materials for use in ballistic vests is likely to focus on several key areas of innovation and optimization. One of the main areas of interest will be the further research and development of modified natural fibers. These fibers represent an environmentally sustainable and cost-effective alternative to synthetic materials, but their inherent properties, such as high water absorption and the presence of impurities, require complex surface treatments. Future work could focus on refining these treatments to improve the mechanical properties of natural fibers and their usability in ballistic applications.

Another key area of development will be advanced composite systems. Composites that combine different materials can provide an optimal balance between ballistic protection, weight, and wearer mobility. Significant progress could be made in this area by using natural fibers with advanced synthetic materials and nanomaterials. Nanomaterials, although less commonly used, offer promising potential for enhancing ballistic performance through the development of nanocomposites that can improve the protective capabilities of ballistic vests.

The development of synthetic fibers such as para-aramid, nylon, and UHMWPE is likely to continue toward addressing their environmental impacts and improving user comfort. Current synthetic fibers, although offering high modulus, impact strength, and resistance to various external influences, suffer from certain shortcomings such as irritation of the wearer's skin and limited moisture-wicking capacity. Future research could focus on minimizing these negative properties while maintaining or improving their protective functions.

Mineral materials such as ceramics and glass fibers are likely to be the next direction in the development of ballistic materials. These materials, while offering a high level of protection against high-velocity projectiles, have the limitations of high weight and stiffness, which negatively affect the mobility of the wearer. Future innovations could focus on reducing the weight of these materials and increasing their flexibility without compromising their protective properties.

Overall, future research and development in the field of ballistic materials is expected to continue in an effort to find innovative solutions that offer better protection while maintaining or improving the comfort and mobility of users. A key challenge will be to achieve an optimal balance between protection, cost, and environmental aspects, ensuring safety, and effectiveness in high-risk environments.

8. Conclusions

This review provides a comprehensive analysis of the evolution and current state of materials used in ballistic protection. It also provides a categorization of body armor into hard and soft variants, which highlights the trade-offs between protection and mobility. While hard armor offers superior defense against high-speed projectiles, its inherent weight and rigidity pose challenges to wearer mobility. Conversely, the advent of soft armor, comprising multiple layers of high-performance fabrics, has introduced a new level of flexibility, albeit with a trade-off in protection levels.

This paper is focused on the exploration of modified natural fibers and advanced composite systems, with a goal to achieve advanced ballistic protection. Moreover, it is focused on traditional materials like metal and ceramic, modern synthetic fibers, and natural fibers. The development of ballistic protection materials is a dynamic field of investigation, driven by the increasing demands of military and law enforcement personnel facing diverse threats worldwide. Natural fibers have many advantages including biodegradability, low cost, and lightweight; however, in their raw state, they have high water/moisture absorption or can contain other compounds like wax, oil, etc. Due to this, it is necessary to modify their surface by adding coupling agents, chemical treatment, enzymatic treatment, or corona/plasma treatment. This improves the connection between polymers and natural fibers.

Natural fibers offer a compelling alternative to synthetics due to their properties such as low cost, lightweight, biodegradability, and good specific strength. However, high water absorption and the presence of impurities require surface modifications to enhance their mechanical properties and overall applicability in high-end ballistic applications. On the other hand, synthetic fibers like para-aramid, nylon, and UHMWPE dominate the market of lightweight ballistic protection, offering high elastic modulus and impact strength, along with resistance to water, stains, heat, and chemical damage. Despite their advantages, synthetic fibers come with ecological concerns and potential drawbacks such as skin irritation and limited moisture-wicking capabilities. Furthermore, the success of ballistic protection heavily relies on factors beyond fiber type, including yarn nature, fabric construction, and layer composition. Composites, mineral-based materials like ceramics and glass fibers, and carbon-based fibers present additional options with their unique advantages and limitations, further broadening the scope of materials available for ballistic applications. Nanomaterials, although less commonly used, offer promising avenues for enhancing ballistic performance through the development of nanocomposites. Generally, the selection of materials for ballistic vests involves a balance of performance, cost, and environmental considerations to ensure optimal protection for those operating in high-risk environments.

The combination of the mentioned materials can achieve an optimal balance between protection, mobility, and wearer comfort, ultimately ensuring safety and effectiveness in high-risk environments. Further research will continue to push the boundaries of material science, exploring innovative solutions such as modified natural fibers and advanced composites to further enhance ballistic protection capabilities.

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