

“APPLICATION OF NANOCELLULOSE IN MILITARY SECTOR: A REVIEW”

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Abstract

The military can put nanocellulose to good use by developing self-repairing and self-diagnosing materials. Nanocellulose is eight times stronger than stainless steel and has ten times the strength of Kevlar. The use of nanocelluloses in the armed forces is the primary topic of this study. Several studies have shown that the military can successfully use nanocellulose as a new green bio-based material; however, the technology still needs some refinement. It has to be put to the test with authentic chemical weapons like Tabun. The economic viability and accessibility of nanocellulose at an industrial scale is another problem. Natural fibers are abundant, providing the armor industry with a low-cost option for meeting the rising demand in the market. However, the NIJ Tier III standard requires that a plate of armor withstand six shots before failing, and this particular type of natural fiber-based hard-shell armor has only been tested for one. Therefore, in order to make armor plates economically feasible, substantial research is required to increase the ballistic performance of multi-layered armor based on natural fibers. None of the numerous review papers on bio-composites that focus largely on their characterization, production, processing, and other uses have investigated the mechanical endurance of body armor systems.

Keywords: Nanocellulose, bio-based material, natural fiber, cost-effective, military, Kevlar, tensile strength, mechanical performance, armor structure.

I. INTRODUCTION

With an estimated total of \$1917 billion, the global military budget in 2019 was up 3.6% over the previous year. The overall expenditure is used for more than just the production of various weapons; it also pays for a significant share of the development of both the uniforms and the weapons themselves. Experts estimate that the United States, Japan, Germany, Turkey, etc. have spent hundreds of billions of dollars on technological development and research. The realization of functionality with the least amount of weight and space is necessary since military power elements are frequently confined by weight, transmission speed, or both. Newer research is progressing quickly to provide the same level of safety. One other method for reducing bulk and weight is to make use of materials that serve more than one function [1]. (Example: a foundation and covert capabilities).

Self-healing and self-diagnosing materials are a potential solution to these issues, since they may boost system resilience while reducing maintenance requirements. Nanocellulose is a substance that has ability for its use in military applications. A nanoscale version of cellulose is the source of this substance. When compared to Kevlar, nanocellulose is eight times stronger than stainless steel when tested for tensile strength. Military applications of nanocellulose are the exclusive topic of this study. Scientific investigation like this will ensure the reliability of the cutting-edge electronics that underpins so many different uses. Nanocellulose may be the best candidate among the aforementioned materials for fulfilling these needs. There is still a great deal of research needed before nanocellulose is used in any commercial setting, but it can be altered and functionalized for various applications. When those nano cells are densely packed together, the benefits of cellulose become much more substantial. This might lead to the production of highly ordered regions from which nanomaterials known as nanocelluloses could be extracted. [1] [2] Two distinct types of nanocellulose exist: (1) nanostructured materials and (2) nanofibers. The origins of the cellulose, the conditions under which it was extracted and manufactured, and any treatments that were applied before or thereafter all have an effect on the structure, size, and other features of each type. Nanocellulose's unique 3-D organizational nanostructure and nanoscale physical and chemical characteristics open up exciting new avenues for research and development. [3]

Packaging, automotive, energy, and other industries are just a few of the many that have shown interest in using nanocellulose, which has gained a reputation as a reliable material. These advances in nanocellulose technology have potential military uses, both on their own and as part of a composite along with other materials. However, the newly produced material must maintain or improve upon the qualities of the materials now used in the fabrication of military applications. [3] For this reason, we have reviewed the existing and future uses of nanocellulose in the defence sector. We've also shed light on nanocellulose's contribution to the enhanced final qualities of the material now seeing military application. [2] [3]

II. LITERATURE REVIEW

Over the last 20 years, the literature about nanocellulose, which is manufactured from a variety of naturally occurring materials utilizing various methods, has been extensively researched. Some obstacles must be addressed, notably in the domains of the top and end-reducing changes, the enhancement of environmentally friendly extraction procedures at lower cost with lower energy-consuming processes, and production upscaling.[4] More research is needed to bridge present gaps in the actual transition between microscale and corporate or economic manufacturing. Nanocellulose has emerged as a new class of materials for high-end military applications such as bulletproof vests and flame-retardant materials, as well as textile industry, electrical industry, and energy applications. It may be synthesized using leftovers from industry, forest and agricultural fibers which has turned into high-value commodities. Numerous studies have demonstrated the use of nanoparticles as a sustainable bio-based fabric in the military, while further research is needed.[5] To ensure that the features developed to truly meet military requirements, R&D should ideally incorporate the actual use of military

technology.[4] Nanocellulose is a form of cellulose but only in the form of nanostructure. It has also been proved to be one of the best green materials in the modern times. Nanocellulose or NC materials have grown interests unsettled to abundance, high viewpoint and better in mechanical properties, sustainability, and nanocomposites. Nanocellulose has the potential to be a completely green nanomaterial due to various remarkable traits such as greater surface area, tail or surface chemical ability, superior mechanical properties, anisotropic form, and so on.[6] It is a superb material with a wide variety of applications in healthcare and materials science, with a great potential for emerging sectors. There is possibility for new implementations and improvements to established ones, which may be used in a variety of sectors that demand sophisticated materials.[5]

Nanocellulose may be produced from agricultural and forestry waste fibers that can be turned into high-value products. Low thermal properties, significant aspect ratio, and high crystallinity are some of its fascinating properties. This review's objective is to convey to readers some of the current buzz around nanocellulose research, the material's remarkable chemical and physical characteristics, and its prospective military applications.^[8] The use of nanocellulose for various military applications is a potentially exciting area for future research and development. Even if the utility has been demonstrated in multiple works, there still need to be certain improvements. For instance, the effectiveness of an antibiotic substance must be evaluated using the well-known biological warfare toxins sarin and tabun. Another issue is the low cost and ease of access to nanocellulose on an industrial level.^[7] Natural fiber reinforced polymer composites, or NFRPCs, are widely used in the construction and manufacturing sectors. Nonetheless, they can be elevated to great structural uses, such as significant structural elements in ballistic and defensive applications.^[1]

Natural fibers with greater kinetic energy collection and dissipation have effectively replaced Aramid and Kevlar material in body armor to increase ballistic performance.^[3] Given the availability of synthetic materials, this industry would be able to supply the growing need for defensive armor on a spending plan. These ecologically friendly solutions would allow combat personnel to employ armor technology more simply and economically, while also minimizing the number of deaths.^[9]

III. NANOCELLULOSE PROPERTIES, CATEGORIZATION AND MODIFICATION

Nanocellulose is a kind of cellulose that is 100 nm or smaller in size. High impact strength, electrical characteristics, low weight, chemical stability and toxicity, and biocompatibility are only a few of its impressive features. It also has a large specific area, high porosity, and considerable pore interconnectivity. Based on cellulose's hydroxyl groups (-OH), nanocellulose may be easily derivatized and have new functions introduced that are useful in many contexts. [10] Hydroxyl groups make up a large portion of cellulose's chemical structure(see Fig. 1). (a). [11] All of these special qualities of nanocellulose are highlighted in Table 1 [12]. Nanocellulose may come in three distinct forms: cellulose nanofibers (CNF), cellulose nanocrystals (CNC), and bacterial nanocellulose (BNC). Nanocellulose

may be found in a wide variety of shapes and sizes, but all of them are nanoscale materials. Figure 1 depicts the CNC, CNF, and BNC topologies that result from many different approaches (b). The other two, CNC and CNF, are derived from plants, while BNC is based on micro- bacterial nanocellulose. CNC and CNF are both derived from plants, and their production requires hydrolysis of the plant cellulose in one of three ways: mechanically, physically, or chemically. BNC, on the other hand, are produced through the use of microorganisms and biotechnology. This process produces hydrogels with properties similar to CNF and CNC, including high purity, mechanical strength, and an interconnected micropore system.

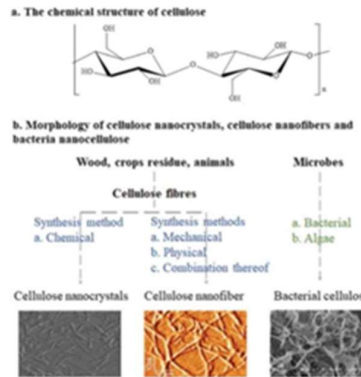


Fig. 1 (a) The composition of cellulose, (b) morphology of bacterial nanocellulose, cellulose nanofibers, and nanocrystals.^[11]

This cutting-edge technology paves the way for the process-controlled production of a wide variety of forms, sizes, surface properties, and nanonetwork topologies. The newly created layered materials have several potential applications, including in the realms of medicine and defense. [13] Klemm and his co-workers demonstrated the potential for using this technique to develop medicines and medical supplies for use in cardiology and intestinal surgery. Through this process, it is able to adapt its behaviour and features to meet the needs of different settings. Oxidative stress, carboxylation, dehydrogenation, acylation, subsequent positioning, and polymer bonding are all examples of surface functionalization processes that may be used to achieve this goal. [14] Surface carboxylation is often used to improve nanocellulose's chemical characteristics.

Attribute	Benefits
Renewable	It is possible to employ biofuels made from sugarcane waste, palm oil production, bamboo shoots, and wheat products.
Biodegradability	It is commonly known that this chemical is biodegradable; it is harmless for the environment; and bacteria may break it down.
Reusable /Reversibility	the capacity to repeatedly desorb or adsorb contaminants.
High Mechanical and crystalline properties	Influences a material's final properties, especially composites.

High Specific surface area	Since it influences adsorption and response processes, it is one of the most important criteria for nanomaterials.
Surface Functionalization	Nanocellulose compatibility is raised via surface functionalization. It is also intended to expand its utility by combining it with other substances such as superconductors, antimicrobials, and fire retardants.

Table 1 The characteristics of nanocellulose [12]

Nanocellulose's surface characteristics and its interfacial compatibility are critical to its performance indicators. This is because increasing the efficacy of nanocomposites necessitates a continuous diffusion of nanocellulose in polymeric composites. How well nanocellulose disperses depends on the balance between charge antagonism and hydrophobic interactions. The dispersibility of nanocellulose may be greatly enhanced by making the necessary changes, such as those indicated above. According to Chu et al., the benefits of hybrids using synthesized nanocellulose outweigh the costs and problems. So, additional research is needed to properly understand the mechanics of nanocellulose dispersion. Figure 2 shows a variety of nanocellulose surface functionalization techniques.

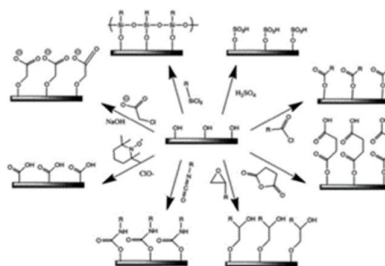


Fig. 2 Common surface functionalization on nanocellulose [15]

Furthermore, a survey was done on the website www.lens.org for the term "functionalization of nanocellulose," and it was observed that the number of articles/research papers based on functionalization of nanocellulose has increased in recent years. As a result, scientists interested in the synthesis process of nanocellulose has grown during the last decade.

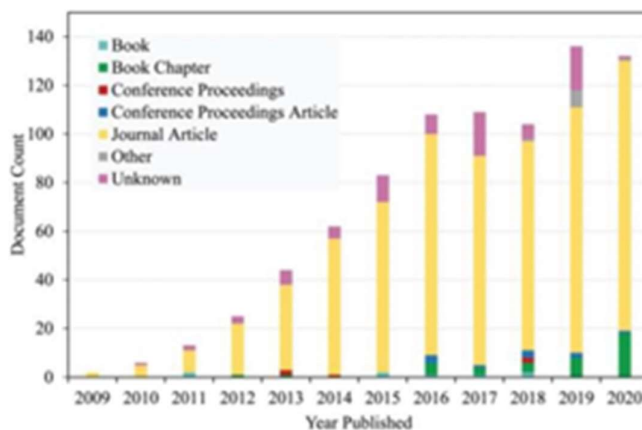


Fig. 3 A summary of articles that have been published and focus upon functionalization of nanocellulose.

IV. APPLICATION OF NANOCELLULOSE IN MILITARY

Packaging Sector

Nanocellulose has been the subject of several research projects because of its potential as a component in a wide range of packaging materials. As was said in the introduction, nanocellulose may be utilized to create packaging that satisfies military specifications for materials that increase defence and durability, ecological acceptability, and adaptability. [16] The mechanical qualities of the material used for military packaging are crucial. Nanocellulose has been shown to improve the mechanical properties of packaging materials. [17] The mechanical performance of common packaging polyolefins like polyethylene, polypropylene, and polyethylene terephthalate may be greatly improved by adding a small quantity of nanocellulose, often between 1 and 5%. The mechanical characteristics of nanocellulose-modified composites are summarized in Table 2.

Polymer Matrix	Nanocellulose Mixture	Improvement in Mechanical Properties
Polypropylene	2.08 wt.%	$\sigma_t - 34.201\%$, $E - 175.901\%$ $\sigma_f - 27.81\%$ $E_{flex} - 88.92\%$
Polyethylene	3.20 wt.%	$\sigma_t - 57.71\%$, $E - 92.71\%$ $\sigma_f - 198.202\%$ $E_{flex} - 25.005\%$
Polyvinyl alcohol/starch	10.5% (v/v)	$\sigma_t - 85.201\%$ while elongation at break decreased
Polyamine/ Epoxy resin	0.75 wt.%	$\sigma_t - 29.902\%$, $E - 66.703\%$ $\sigma_f - 30.603\%$ $E_{flex} - 21.404\%$
Poly (styrene-co-butyl acrylate) copolymer	10 wt.%	$E - 6142.01\%$, $\sigma_t - 104.2\%$ and elongation at break decreased.
Polycaprolactone	3 – 12 wt.%	Little increase in strain at break and tensile modulus while maintaining tensile strength

σ_t – Tensile Strength; σ_f – Flexural Strength; E – Young’s Modulus; E_{flex} – Flexural Modulus
Table 2 Mechanical properties of nanocellulose reinforced composites

Energy Devices

For its own unique reasons, nanocellulose stands out as a promising material for use in electrochemical energy storage devices (EES). Nanocellulose's unique features, especially its strong electrochemical capabilities, make it a promising candidate for use in cutting-edge energy technology. Nanocellulose's mechanical qualities may be used to great effect

as a structural matrix in polymer electrolyte composites. [18] Nanocellulose's outstanding interwoven structure also makes it a useful scaffold for building electrode hosts, which improves ion transport and, in turn, the performance of the electrode cycle. Because nanocellulose is not electrically conductive, it must be functionalized with conductive polymers, metal particles, or carbon compounds such as graphene, soot, and carbon nanotubes. The improved nanocellulose-based EES has the potential for use in military applications because of its adaptability, low weight, and durability. In addition, the military has shown a lot of enthusiasm for rechargeable gadget technologies. [19] Nanocellulose is used in a variety of energy storage (EES) technologies, such as ultracapacitors, solar cells, and devices used to recharge lithium-ion batteries. Nanocellulose has found several uses in military energy applications, including lithium-ion batteries, solar panels, and energy storage systems.

Fire Retardant Material

Increased utilization of nanocellulose blends that are fire retardant or flame resistant is being seen in cutting-edge industries. Nanocellulose-reinforced thermoset nanocomposites were investigated for their fascinating flammability properties. Nanocellulose composites do well when put through fire tests, giving off less smoke and potentially harmful compounds. New military hardware, buildings, and ecosystems are all saved, and most significantly, lives are saved thanks to their efforts to put out fires. Nanocellulose composites include fire-resistant fillers and additives such as halogen, oxalic acid, iron, mineral deposits, and micro- and nano compounds to prevent or lessen the effects of a fire. [20] Nanocellulose may be treated with flame retardants in two ways: solution impregnation and surface treatment. Nanocellulose composites were sometimes combined with polyurethane to create fireproof materials.

Propellant

Nanocellulose may be used to create military propellants with a larger energy density per mass than conventional incendiary device. The functionalization of nanocellulose is essential for its use as a propulsion system. Numerous research efforts and innovations have been dedicated to the process of creating nanocellulose as a fuel. By using nanocellulose, Zhang et al. created a dual solid-based propellant. [21] [22] As double-base propellants, they perform very well because of their hydrophilic nature, high aspect ratio, and improved suspension stability compared to traditional double-base propellants. The breaking strengths under tension and elongation both rose by around 34% and 45%, respectively. A drop in pressure coefficient of 20% was achieved, while a boost in propellant burning rate of 27.5% was achieved. [23]

Military Medical

Nanocellulose is already being used in a variety of medicinal applications, including bioengineering, bone scaffolding, tissue repair, and drug research. Fig. 4. In this area, nevertheless, only military-related applications were addressed.

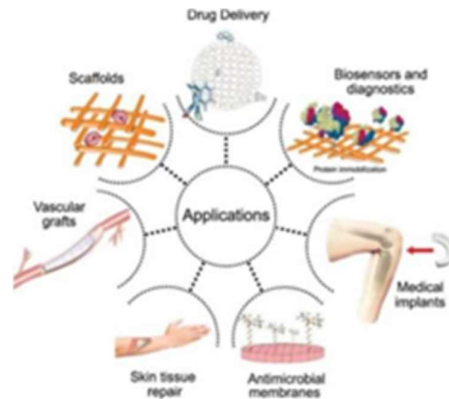


Fig. 4 Medical applications of nanocellulose

V. CLASSIFICATION OF NATURAL FIBERS AND MANUFACTURING TECHNIQUES

The extraordinary qualities of natural fibers are seen in many different fields. Because of their superior mechanical properties and biodegradability, natural fibers are gaining prominence, especially in the automobile sector and for more fundamental applications. Furthermore, several academics are stressing the need to use recycled materials in their investigations. [26-28] The plastics sector has greatly benefited from the increased interest in the development of new and better materials brought about by the expanding need for technical components. Traditionally, the thermoplastics industry has employed natural materials primarily as reinforcement for ecological composite products. [27] For several reasons, including their superior sustainability, eco-friendliness, and renewable resource potential compared to low-cost microfiber-reinforced plastics, natural fibers are quickly gaining popularity. As a bonus, reinforced composite compounds made from basic architectural polymers have found widespread usage in several industrial settings. [29] These fibers have a unique structure made up of a cellular wall that is triangulated into three sections. The position and angle of the small fibrils within the cell wall regulate the fibrous properties. The cell wall is composed of two layers: the primary cell wall (S1) and the auxiliary cell wall (S2). Throughout a plant's life, the primary cell wall continues to spread. [28] There are three distinct layers to the auxiliary cell wall, and inside each lies a string of microfibrils. Hemicellulose molecules, which are net-like in both form and substance, adhere to cellulose strands. Lignin and pectin provide adhesion, whereas cellulose and hemicelluloses form a network. [29-31] Cellulosic fibers' strength and rigidity come from their adhesive qualities. How well fibers retain their engineering qualities over time is a function of their secondary layer (S2). For example, increasing the amount of cellulose and decreasing the angle of the cellulose microfibrils are common ways to make materials stronger. In Table 3, we compare the engineering qualities of natural and synthetic fibers. Figure 5 is a schematic showing the structure of natural fibers.

Fibers	Density (g/cm ³)	Tensile Strength (MPa)	Elongation at Break (%)	Tensile Modulus (GPa)
Sugar Palm	1.4	160.01	8.01	4.96
Bagasse	2.0	305	-	17
Bamboo	1.3	135-250	-	11-17
Flax	0.8-1.4	400-1090	2.5-3.7	27.6
Jute	1.8	395-780	1.4-2.1	26.5
Kenaf	1.9	245.5	1.7	53
Aramid	1.9	3000-3250	3.25-3.84	63-67
Kevlar	2.54	3400	2.45-3.82	60

Table 3 Physical and mechanical performance of natural fiber vs. synthetic fiber.

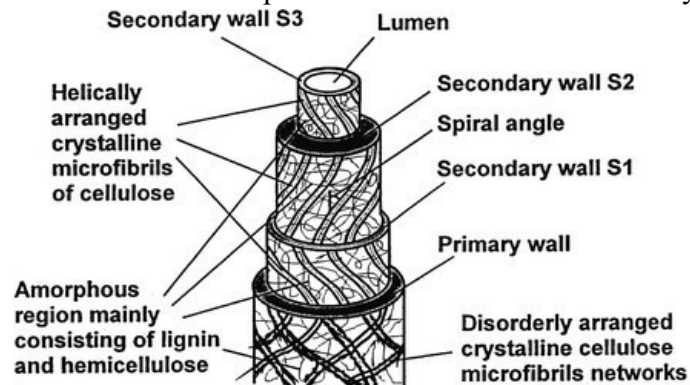


Fig. 5 Structure of Natural Fibers

Raw natural fiber has various drawbacks that make it incompatible with polymers, including a high moisture percentage, dead cells, wax, and oil. The solution is to modify their outer layer. The primary goal of surface functionalization is to increase the durability of composite systems by improving the qualities of natural fiber. Chemical, enzymatic, corona, plasma, and coupling agent treatments are all viable options for modifying surfaces. These treatments focus on the amorphous part of cellulose to enhance the contact between the fibers and the matrix. The amorphous part of cellulose has a high concentration of hydroxyl groups, giving the fiber a polar character and reducing its ability to interact with the matrix. So, surface morphology was used to reduce or eliminate hydrogen bonds, which improved adhesion to the matrix and the mechanical characteristics of the fiber. Plants that are used to make natural fibers fall into one of two categories: main and secondary (Figure 6) [25]. Cotton, jute, kapok, hemp, kenaf, and sisal are all examples of "primary plants," whereas "secondary plants" include bananas, coconut coir, pineapples, and oil palms. Every year, over 30 metric tonnes of natural fibers are generated and use as raw materials or by-products in countless different industries, such as those that make clothes, packaging, paper, cars, buildings, and sports goods. Materials manufactured from animal fibers, as opposed to plant fibers, might include wool, silk, feathers, feathery fiber, and animal hair. Natural fibers have been utilized for centuries in many developing nations. Higher interfacial adhesion occurs between components due to the poor interaction between the fiber and the adjacent moisture content when cellulose

levels are low. As a result, it is better suited for heavier ballistic applications in general. Table 4 details the wide variety of polymer composites that may be used for ballistic applications and whether they are reinforced with natural or synthetic components. [25]

Hybrid Natural Fiber/Synthetic Fiber	Polymer Matrix	Remarks
Carbon Aramid	Epoxy	Using different layer for each sample
Woven Kenaf & Kevlar	Epoxy	Using Amine Hardener
E-Glass Fiber	Epoxy	Single fiber diameter of 14e16 mm was used. E-glass fibers were sized using epoxy silanes of max. 0.4% by weight
Kevlar	Thermosetting Resin	Avg. fiber weight fraction of 75% for each sample
Woven Fabric	Unsaturated Polyester Resin	Using 50% Fiber Volume
Aramid & Kevlar	Epoxy	Using plain Kevlar

Table 4 Types of hybrid natural fiber/synthetic fiber reinforced polymer matrix use in ballistic application. [25]



Fig. 6 Various Types of Natural Fibers [25]

Despite competition from natural fibers throughout the years, the market for synthetic fibers is currently unchallenged. There has been a resurgence of interest in using natural additives, especially in the automobile sector. Natural additives are being used to replace glass fiber. Natural fiber has essentially supplanted synthetic fiber in high-performance materials, such as those used in the automobile and aerospace sectors. To promote the use of natural textiles, the German car industry plans to produce bio-renewable components. Due to their environmental and economic benefits over synthetic reinforcing materials, natural fibers have attracted the attention of academics and engineers. When used in

composites, natural fibers improve degradability and reduce pollution. [29] They are preferred since their usage has a less negative effect on the environment and people's health. Producing natural fibers requires just around 17 percent of the energy needed to manufacture man-made fibers like glass fiber. [27] Prior research has compared the ballistic properties of NPP composites (natural fiber-reinforced polypropylene composites) to those of NPP composites with metal plates as the approaching and backing material. The research looked at the performance of natural fibers, including flax, hemp, and jute. [29] By using compression molding, we were able to create composites with a fiber volume fraction of 46%. A sufficient amount of study was also done to understand the failure mechanisms caused by hybridization. This demonstrated that shearing, delamination, and fiber breakage were all more likely to occur at the point of contact. [30] For their study, Monteiro et al. investigated the ability of a singular herbal fiber derived from the figue shrub to be used in plastic composite-sponsored MBAS. Researchers discovered that polyester resin's thermal and viscoelastic characteristics improved when fiberglass fibers were mixed in. [33] The sand mold depression was 15 mm deep for the polyester/Kevlar composite and 23 mm deep for the fiberglass/polyester composite.

According to the price estimates of industry professionals, polyester/fiberglass composite MBAS would be 13 times less expensive than MBAS built of polyester/kevlar composite. The hybrid composite research analyzed the ballistic impact parameters of polypropylene-based reinforced composites with 2D/3D Kevlar and basalt fiber. [32] The two types of composites made by the symmetric and asymmetric stacking processes When basalt and Kevlar threads were used to weave fabric, a hybrid was created. A 9 mm full metal jacket bullet, made up of a lead core and a brass jacket, was used in ballistic impact testing at velocities ranging from 365 to 435 meters per second. There was a barrage of gunfire [3] onto both laminates. The non-symmetric laminate had basalt fabric on one side and 3-Dimensional Kevlar fabric on the other. [3]

VI. CONCLUSION & FUTURE SCOPE

As a result of technological advancements, nanocellulose is now suitable for use in creating sustainable alternatives in several industries, including packaging, biomedicine, composites, papermaking, water purification, and cosmetics. Identifying and fixing problems is crucial to the widespread adoption of nanocellulose products suitable for a wide range of uses. Nanocelluloses' commercial manufacturing depends on the demands of a broad range of consumers, and the product's widespread adoption might contribute significantly to the acceleration of global technological progress. Several recent developments in using nanocellulose for military objectives were reviewed. Research in this area may be furthered to enhance nanocellulose's usefulness as a weapon component. While several studies have shown nanocellulose's usefulness as a biobased material with military applications, further progress is needed. To add insult to injury, any nanocellulose-based filtration materials developed must be tested with authentic chemical

warfare agents, including sarin, tabun, cyanides, and chlorine. The budget and unavailability of nanocellulose on an assembly line are also major issues. Several publications have achieved headway toward their goals of increasing efficiency and decreasing the cost of nanocellulose synthesis, which bodes well for its eventual broad use. New advancements in the use of nanocellulose in the military were discussed. Several studies have shown that the military can successfully use nanocellulose as a new green bio-based material; however, the technology still needs some refinement. It must be put to the test with authentic chemical weapons like Tabun. The economic viability and accessibility of nanocellulose at an industrial scale is another problem. Natural fibers are abundant, providing the armor industry with a low-cost option for meeting the rising demand in the market. However, the NIJ Tier III standard requires that a plate of armor withstand six shots before failing, and this particular type of natural fiber-based hard-shell armor has only been tested for one.

For this reason, armor plates cannot be made economically feasible without substantial study into increasing the ballistic performance of multi-layered armor based on natural fibers. Although there have been several review manuscripts on bio-composites, each focusing solely on different aspects of these materials, from characterization to manufacturing, processing, and other uses, none of these reviewers have been able to develop bulletproof vest structures.

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