Personal protective clothing is intended to protect the wearer from various hazards (mechanical, biological, chemical, thermal, radiological, etc.) and inhospitable environmental conditions that may cause harm or even death. There are various types of personal protective clothing, manufactured with different materials based on hazards and end user requirements. Conventional protective clothing has impediments such as high weight, bulky nature, lack of mobility, heat stress, low heat dissipation, high physical stress, diminishing dexterity, diminishing scope of vision, lack of breathability, and reduced protection against pathogens and hazards. By virtue of the superlative properties of graphene, fabrics modified with this material can be an effective means to overcome these limitations and to improve properties such as mechanical strength, antibacterial activity, flame resistance, conductivity, and UV resistance. The limitations of conventional personal protective equipment are discussed, followed by necessary measures which might be taken to improve personal protective equipment (PPE), the unique properties of graphene, methods of graphene incorporation in fabrics, and the current research status and potential of graphene-modified performance textiles relevant to PPE.

1. Introduction

Increasing worldwide concern about the work health safety of people from different professions, particularly emergency responders has made personal protective equipment (PPE), especially new performance textile fabrics as protective clothing a growing focus of research. According to safe work Australia, “PPE refers to anything used or worn to minimize risk to workers’ health and safety.” Emergency responders (health care workers, law enforcement, defense, paramedics, and firefighters) play a significant role in protecting society in case of emergency situations such as natural disasters, epidemics, fire, or terrorist attacks. They may deal with diverse hazards, ranging from chemical, mechanical, biological, physical to electrical, and put themselves at high risk of harm or even death at work. Protective clothing’s act as a barrier and protect the wearer from health hazards, thus is effective in diminishing occupational injuries and economic loss.

If protection from contaminants is required, protective clothing should cover the entire skin, should be easy to wear, easy and safe to remove, and comfortable to use during work. Selecting the appropriate protective clothing according to the level of risk is fundamental to protect wearer from hazards. However, the problem with most PPE is that higher safety can only be ensured with higher costs, physical discomfort and strain such as diminishing flexibility, deftness, comfort, and vision. Some other intrinsic dangers of conventional PPE include heat stress, lack of mobility, fall hazard, seizures, physiological malfunction, or anxiety. Although PPE has benefitted from various high technology innovations, there remain many challenges and areas for improvement. An ideal protective cloth should protect from hazards, without sacrificing the comfort and ability of the wearer to carry out essential tasks.
Graphene, a 2D, single layer planar sheet of sp²-bonded carbon atoms, has proven itself as a ground-breaking material in diverse areas of technology owing to its exceptional mechanical, thermal, chemical, electrical, and antimicrobial properties. These extraordinary properties render it an attractive material with potential for diverse technological applications and advantages over other comparable materials. The most promising approach to utilize the unique properties of graphene is to use it in composite materials. In recent years, development of new property textile fabrics with multifunctional activity has gained a lot of interest. Incorporating graphene or graphene derivatives into polymers/textiles can improve the properties of fabrics for specific applications. Graphene incorporation into fabrics or modification of a textile surface by graphene can not only improve mechanical strength, flame-resistance, conductivity, antibacterial activity, resistance to abrasion, and UV-protectivity but also prevents the diffusion of heat and gases. Graphene-based woven fabrics also exhibit excellent flexibility. All these qualities could be added to PPE textiles in one lightweight application (Figure 1) if textile fabrics could be modified by graphene/graphene derivatives. Therefore, graphene modified new performance textile fabrics may be the breakthrough to overcome the shortcomings of personal protective clothing.

Recently, a few researchers have reported on graphene modified fabrics with different techniques. However, no review has been conducted on graphene modified personal protective equipment clothing till date. The objectives of this review are to identify the limitations of present PPE, measures which can be taken to improve PPE and identify the research evidence supporting the use of graphene in modified new performance textiles relevant to PPE.

2. Limitations of Currently Used Personal Protective Equipment (PPE) for Emergency Responders

It is essential to confirm the right type of PPE with desired functional properties for the risk that the wearer is exposed to. Despite many advancements, there are many shortcomings of PPE for emergency responders. Limitations and present conditions of PPE are described below pertaining to specific occupational groups and their needs.

2.1. PPE for Healthcare Workers (HCWs)

Infectious diseases epidemics and pandemics are a major health and safety concern for health care workers (HCWs). One of the hierarchy of controls for protecting both patients and HCWs from transmissible pathogens via exposure to body fluids and bioaerosols is use of appropriate PPE, especially when no actual treatment or prophylaxis is available for the disease in question. In the initial stage of an outbreak, drugs and immunizations may be inaccessible or deferred in development. In that case, such as the 2014 Ebola epidemic, PPE is the only available intervention to protect HCWs from acquiring infectious diseases.
HCWs died (over 900 cases and 500 deaths) during the Ebola outbreak in West Africa in 2014. The environment was extremely hot and humid, and HCWs perspired profusely in their suits, limiting their ability to work in PPE for more than 30 min. During the Ebola outbreak, HCWs used different types of PPE (Figure 2), such as shoe covers, tychem suit, tyvek micro-clean hood, respiratory protection, eye protection, and double gloves. The heavy weight of these PPE and the low air permeability of the clothing caused insulated conditions, and significant heat stress, with body temperature increasing in HCWs. Heat fatigue may have contributed to HCWs becoming infected due to exhaustion and mistakes while removing PPE. PPE in such conditions may be impregnated by sweat, moist air, condensation throughout breathing, or body fluid contact during use.

Many researchers suggest that textiles used in PPE may act as vehicle for the acquisition and spreading of microorganisms. Soft surfaces of apparel are often contaminated with pathogens that can cause infectious diseases. Pathogens grow well in moist conditions and in protein-enriched biological waste that might be present on HCW PPE. Pathogens can survive on the PPE, which can be dangerous for HCWs and patients. A study inoculated different fabrics (cotton, cotton-polyester, polyester, polypropylene) with various gram-positive bacteria and the pathogens were able to survive from 1 to 90 days on fabrics and plastic surfaces.

Some research has been done on improved PPE design after the 2014 Ebola outbreak, but improvement of protective clothing has been overlooked. Advanced textiles fabrics should have fluid repellent property and incorporate antimicrobial activity to minimize the growth of contagious microorganisms on the protective clothing surface. Researchers can also explore different materials and fabrics that can minimize the retention and spread of infective biological hazards originating in body fluids.

**2.2. PPE for Fire Fighters and Laborers**

Workplace injuries are the main source of disabilities globally. Firefighters work in dangerous superheated conditions that are
not only physiologically but also mentally stressful. As one of
the riskiest occupations, firefighting is associated with a high
number of injuries. Firefighters endured wounds and limited
versatility because of failing to control their balance (slips or
falls).[24] During firefighting sometimes firefighters may be
exposed to polycyclic aromatic hydrocarbons (PAHs) and other
toxic chemicals.[25]

While firefighting in hot and humid environment against
multiple hazards (thermal, chemical, toxic gas, physical
injuries, etc.), firefighters need flexibility in movement and
motion. Heavy PPE (Figure 3) including personal protective
clothing, helmet, mask, self-breathing device, gloves, boots,
etc., limit firefighter’s mobility and comfort. Firefighters
can experience physiological strain and tiredness because of
the high weight and bulky nature of PPE. They may also
face cardiac stress, low breathability, accumulated sweat, and
humid hot conditions.[16]

Son et al. did a study on protective clothing of Japanese
firefighters. The study concluded that aluminized fire jackets
had inferior ventilation and flexibility, and aggravated heat
strain more than the nonaluminized. However, nonalumin-
ized jackets were worse for water resistance and maintain-
ability. It restricted body movement and caused muscle fatigue
while firefighting.[27] Again, wildland firefighters do their duty
in adverse conditions and are exposed to both sun and flame
radiation.[28] In heat stressed conditions, PPE can dramatically
reduce their performance by reducing heat transfer and sweat
evaporation.[29] This is exemplified in the work undertaken by
Carballo-Leyenda et al.[30] They found that PPE led to a low
perspiration evaporation rate, which increased the thermophys-
iological response of wildland firefighters and reduced perfor-
mance by around 50%.[30]

The firefighters protective clothing should not only protect
from heat and hazards but also help the dissipation of internal
accumulated heat.[31] This view is supported by Lee et al., who
surveyed firefighters’ desire for next generation PPE and found
that the preferences were for smart features with location mon-
toring and an automatic body cooling system.[26d] The primary
focus in the development of cutting-edge PPE fabrics for fire-
fighters ought to be the development of basic and light mater-
ials that bolster the performance and safety while not reducing
protection.

2.3. PPE for Law Enforcement and Military Personnel

Law enforcement personnel may be the first to respond to an
event, therefore have the least forewarning about potential
hazards.[32] Injuries to military personnel could be more serious
and fatal than those in the general population due to the char-
acteristics of military activities.[33] Police, however, are less well
prepared in the use of PPE, yet may be exposed to chemical
or biological agents when raiding premises suspected of har-
boring drugs, weapons or other illicit goods. The hazards they
face may be uncertain. During the 2018 Novichock attack in
London, the first police detective to enter the premises became
poisoned despite wearing some PPE. With increasing conver-
gence of technologies accessible to criminal, exposure to chem-
ical weapon, and biological hazards at the frontline will be an
increasing concern for police.[34]

Protection of first responders from weapons of mass destruc-
tion (WMD) is a matter of major concern. To protect people
from the harmful effects of biochemical hazards, radiological
exposure, and high-explosive weapons, appropriate technologi-
cally advanced PPE is a critical component. First responders
who endure the initial effect of WMD rely on PPE, availability
of appropriate disinfecting and proper treatment.[35] When on
duty law enforcement personnel must deal with various kinds
of hazards, thus need high level of personal protection. How-
ever, police have less of a culture of PPE use than firefighters
or the military, and wear less PPE because of their continuous
movement and patrol.[14] Kim et al. studied the impact of PPE
on injury occurrence among the military of Republic of Korea
and concluded that a higher number of injuries occurred
among individuals who were not wearing PPE because of uncomfortable feeling and reduced mobility. Due to bulky nature, heavy weight, agonizing sensation, and reduced movement they do not wear PPE routinely.\[36\]

Therefore, the demand for protective light weight, multi-functional flexible garments for military/police is continually increasing.\[37\] In this era of potential biochemical violence, we cannot always predict the risk of exposure for first responders such as police or military. Therefore, advanced research and other studies on various fabrics should be done to develop advanced PPE as suitable protective measures.

3. Research Priority Areas for PPE

The protective clothing should be appropriate for the wearer. They should have dependable barrier protection and resilience. Personal protective clothing also should have ease of cleaning and maintenance, good donning and doffing characteristics, correct design, and most importantly should be comfortable when worn for extended periods of time. Based on the hazard assessment and problems faced by emergency responders the research priority areas of PPE can be determined. To protect emergency responders LaTourrette et al. have outlined the priority areas for improving PPE based on overview of the needs of emergency responders.\[14\] The key priority areas are ensuring comfort by diminishing physical strain and developing effective protective clothing and guidelines to protect from biochemical hazards. The research priorities and necessary measures to be taken are mentioned in (Table 1).

4. Materials Used for Personal Protective Clothing

A single item of protective clothing cannot protect from all hazards. Variables such as duration and type of exposure, level of hazard, type of risk, barrier penetrability, comfort, required time wearing PPE, workplace temperature, and humidity are key factors for selecting appropriate materials, materials composition, assembly, and other specifications of protective clothing. Moreover, the comfort and performance of protective clothing depends on the type of materials, material composition, material properties, thickness of fabric layer, number of layers, heat and moisture transfer mechanism, etc.\[38\]

Various types of materials such as polymers and fibers are used in different protective clothing. In most of the protective clothing the base material is coated by different materials from both inside and outside, thus ensuring optimal protection against exposure to hazards.\[39\] Generally butyl rubber, neoprene, polyethylene or polyvinyl chloride are coated on to fabrics to make the protective clothing impermeable to chemicals, liquids, and vapors.\[38e\] The common materials that are used in protective clothing include:

- Polyamide (nylon and aramid) aramid: Aromatic polyamide is used as base material for fire jackets and fire pants. Both para-aramid and meta-aramid polymers are useful in protective clothing. Good mechanical strength and nonflammable nature make para-aramid suitable for ballistic protection and high temperature shield. On the other hand, meta-aramid is specifically used for its excellent thermal stability. The common trade names of aramid based materials that are used...
for protective clothing are Kevlar, Nomex, Twaron, Corex, Technora, Trellech, etc. \cite{27,29,40}

- Polyethylene: Ultrahigh molecular weight polyethylene having high modulus, strength, and chemical resistance are used to prepare splash resistant garments. \cite{37} Tyvek clothing is made from high density polyethylene nonwoven fibers. DuPont-Tyvek has exclusive ability of permitting vapor to penetrate, while at the same time blocking penetration of water and air. \cite{15} Dyneema, Spectra, and Tekmilon are other available trade names of polyethylene materials for protective clothing. \cite{40}

- Nonwoven fabrics: Nonwovens are gaining significant interest for manufacturing PPE to improve the safety and comfort of workers. Polymer nonwovens have various applications because of their morphology, hydrophilic, or hydrophobic nature, and easy structure alteration techniques. Recently there has been an upsurge in the demand for specialized nonwoven product. \cite{42} Spun-bonded olefins are most commonly used nonwoven fabric manufacturing. Polyethylene nonwoven and pulp/polyester are the foremost materials used in nonwoven protective clothing. Polyethylene nonwoven and pulp/polyester are the foremost materials used in nonwoven protective clothing. Tychem clothing is made of nonwoven polyester, squeezed in between nonhalogenated fabrics with high mechanical strength. \cite{43}

- Phenol-aldehyde: Fabrics made of cured phenol aldehyde (Novoloid) possess high resistance to fire, acids and chemicals. Novoloid has been used for manufacturing hybrid materials for protective clothing. \cite{40}

- Melamine: Melamine based fibers (trade name: Basofil) are very stable at high temperatures, thus found an application in fire fighters protective clothing. \cite{13,44}

- Cellulosic material: Flame retardant and thermal resistant cotton fabric (trade name: Proban) has been widely used as protective clothing for first responders. \cite{45} Again, normal cotton, as well as mixtures of cotton and polyester fabrics are widely used as protective clothing of healthcare workers, doctors and patients in hospitals.

- Tetrafluoroethylene (TFE): Polytetrafluoroethylene has good thermal and chemical stability but possesses low mechanical strength. It is used in protective clothing by mixing with other materials. Gore-Tex and Teflon are trade names of tetrafluoroethylene fabrics. \cite{40}

- Polyester: Polyester is widely used material for protective clothing. Alike propylene and polyethylene, polyesters are also used to manufacture chemical and gas impermeable HazMat suits. Trevira are Sympatex are available brands of polyester. \cite{40}

- Phase changing materials (PCM): PCMs are used to boost the thermal performance of the protective clothing to lessen heat stress. \cite{46} PCMs are microcapsules that are capable of changing phase to approximate the temperature range of human skin. PCMs can be coated on fabrics or can be incorporated into fabrics to control the temperature. Eicosane encapsulated within melamine-formaldehyde, sodium sulfate (dehydrate), and Galactitol are three typical examples of PCM used in protective clothing research. \cite{13,46,47}

- Activated carbon: Activated carbon or activated charcoal coated fabrics are used for the protection from heat stress, chemicals, and reduction of volatile organic compounds for their excellent adsorption capacity. \cite{38,44,48} However, they possess poor mechanical strength. \cite{49}

- Miscellaneous: Some other fibrous synthetic materials like polyethylene benzobisoxazole, polyimide, polybenzoxazole (PBO), polyethylene naphthalate, polyurethane, oxidized polycrylonitrile, and polyetheretherketone are applied in protective clothing for their thermal and chemical stability. \cite{13,40,44,50} Polyurethane can be used as semipermeable moisture barrier into the protective clothing. \cite{44} Organic and metal electroconductive fibers are used in protective clothing to make it antistatic. \cite{40} Resins impregnated with fabrics can increase the mechanical strength of protective clothing. \cite{51} In recent years, due to thermal insulation properties, light weight aerogel nonwoven composites have been used in fire protective clothing instead of conventional dense, weighty, and multilayer clothing. \cite{47,52}

Based on a materials perspective, protective clothing is expected to fulfill two competing demands. Protective clothing must block heat, chemicals, and toxins, be mechanically strong while being lightweight, comfortable, and thermal dissipative. \cite{51} The materials used conventionally cannot satisfy all the requirements simultaneously. So, to ensure safety and functionality, there is scope for further research on multifunctional materials which can solve the limitations of existing materials.

Table 1. Overview of PPE research priorities based on emergency responder direction. \cite{14}

| Research priorities | Problems faced by responders | Necessary measures |
|---------------------|------------------------------|--------------------|
| Ensuring comfort by diminishing physical strain | • Reduced mobility and muscle fatigue | • Reduction of bulky nature and heavy weight |
|                     | • Heavy weight | • Bolstering air penetrability and breathability |
|                     | • Low flexibility | • Increasing of ergonomic features |
|                     | • Agonizing sensation | |
| Develop effective protective clothing and guidelines to protect from biochemical hazards | • Infectious microorganisms | • Ensure proper heat dissipation and transfer |
|                     | • Hot and humid environment | • Ensure protection from microbial and chemical attack |
|                     | • Chemical attack | • Designing PPE to avoid intrusion with responder activities |
|                     | • Explosive weapons | • Smart location monitoring system |
|                     | • Internal heat accumulation | • Training about different hazards and their protection |
|                     | • Inferior ventilation | |
|                     | • Physiological disorder | |
|                     | • Sweat impregnation | |
5. Graphene and Derivatives

Although various types of materials are being exploited for manufacturing different types of protective clothing, there is a gap between expectation and reality. The materials used conventionally have both strengths and limitations. Graphene modified fabrics with its multifunctional properties may be a solution in the field of protective clothing.

Since its discovery, graphene and its derivatives (graphene oxide, GO, and reduced graphene oxide, rGO) have promised several potential applications, which can be applied into everyday life.[54] Graphene is a 2D, single layer monoatomic-thick hexagonally arrayed honeycomb lattice like material of sp²-hybridized carbon atoms. Graphene has some unique thermal, electrical, mechanical, and chemical properties, which made it a suitable material for diverse applications.[55] Delocalized π state bands over carbon layer, which initiates from 2p orbitals are mainly responsible for the properties of graphene.[56]

GO and rGO are the most important derivatives of graphene (Figure 4). GO as oxidized modification of graphene, is monomolecular sheet of graphite consists of numerous oxygen bearing polar functionalities (epoxide, carbonyl, carboxyl, and hydroxyl groups). Due to the polar groups in its basal pinacoid, GO is hydrophilic in nature, which permits improved interfacial bonding with different fibers and polymers. This bonding of GO with fibers helps for enhancement of different functional properties.[55c] As functional groups can interact with each other, the polar groups can be modified by appropriate coupling agents to enable improved interactions with other polymers.[58] Good dispersibility and hydrophilic nature of GO, enables it to smoothly interact with polymeric fibers. However, due to oxygen functionalization GO has some inferior functional properties than pristine graphene, which can be restored by reduction.[57b,59] GO is transformed into rGO by elimination of most of the oxygenated functionalities by chemical, thermal and microwave treatment. Chemical reduction is preferable by most researchers as thermal method is not cost effective.[59a,60] rGO sheets loose its hydrophilic nature after removal of oxygen containing functional groups.[55c] rGO may provide various functions to textiles, including electrical conductivity and electrothermal performance.[61]

6. Unique Properties of Graphene/Graphene Derivatives in Relevant to Protective Clothing

Graphene came into focus when Geim and Novolosev first prepared and characterized graphene by facile “Scotch Tape method.”[62] This simple isolation technique of pristine graphene, made easy to measure, quantify, and characterize its unique properties. Graphene is world’s first 2D material. It is highly optically transparent, very thin (about 1 million times thinner than human hair), has large surface area and light weight.[63] These superlative properties have made graphene an attractive material with enormous potential for industrial application.[64] The main unique properties of graphene are briefly outlined below.

6.1. Mechanical Properties

Graphene is the toughest material in terms of tensile strength. A single layer of graphene is 200 times more resilient than steel. The Young’s modulus and inherent strength of graphene are 1 TPa and 130 GPa, respectively.[57b,64] Owing to this impressive toughness, strength, and stiffness, graphene can be used individually and in composite reinforcement. This strength can be used in graphene modified composites. It is stretchable and flexible.[64b,65] Thickness (higher strength with lower thickness) and purity of graphene layers has a major impact on the mechanical properties.[63a,65]

6.2. Thermal Conductivity

Findings from researchers reveal that photon transportation is mainly responsible for graphene’s thermal conductive behavior, which is ten times greater than copper.[57b,66] Ballistic conduction and diffusive conduction are responsible for thermal conductivity of graphene in low temperature and high temperature condition respectively.[67] Phonon scattering and localization originated by imperfections of graphene is responsible for the inherent thermal conductivity of graphene.[67,68] It is reported that there are differences in in-plane and out of plane conductivity, which is due to sp² covalent bonding and van der Waals bond, respectively.[68] In normal temperature and free state, the
in-plane thermal conductivity varies from 2000 to 4000 W m$^{-1}$ K$^{-1}$, which is maximum among our any known materials.[69,70] However, graphene’s thermal conductivity can be fallen in contact with substrates.[71] Because of superior joule heating, thermal conductivity of graphene spreads heat and generates thermal transmission for passive cooling. This property can transmit heat from the human body to the environment.[72]

6.3. Chemical Activity

Pure graphene sheets are normally inert to chemicals.[63a] They have excellent chemical resistivity and gas impermeability due to their physical structure, thus immune to aggressive environmental conditions. Surface chemistry and thickness of graphene plays important role in graphene sheet reactivity.[63a,64a,73] Bi- or multilayer graphene is much less reactive than single layer.[74] Chemically graphene is very tuneable and can be made reactive by functionalizing via introducing covalently bonded reactive species (such as hydroxyl, bromine, carboxyl, amino, etc.).[7,57b]

6.4. Flame Retardancy

Graphene has good flame-retardant properties.[75] Due to extraordinary lamellar barrier effect, graphene can impede the infusion of pyrolysis products, flammable gases, and oxygen.[76] Graphene materials produce a consistent dense layer when exposed to fire, thus act like a barrier and restrict the passing of pyrolysis products from substrate. Graphene can also act as platform for catalysis and carbonization for some metal oxides.[77] Oxygen-bearing functional groups on the surface, give GO some extent of inherent fire retardancy too.[78] Graphene can also be doped with or mixed with other additives to enhance their flame retardancy.[75,77a,d,79]

6.5. Electrical Conductivity

High movement of π electrons in graphene has made it more electrically conductive than copper.[80] Graphene has very high charge carrier mobility (2000–5000 cm$^2$ V$^{-1}$ s$^{-1}$).[62] It can show electrical conductivity at various temperature range and magnetic field. Due to its high electrical conductivity, graphene can be widely used in smart textiles. Substrate and graphene layers number are also important factors for conductivity.[62,63,65]

6.6. Antimicrobial Properties

Graphene[81] and graphene oxide[82] is an antibacterial nanomaterial (Figure 5). Studies have shown the disinfection capability by graphene derivatives.[83] Graphene and derivatives have antibacterial activity by means of physical contact interaction with bacterial membranes using electron movement of graphene, efflux of cytoplasmic materials, decreasing metabolism, ruinous extraction of lipid, photothermal ablation mechanisms, oxidative stress creating reactive oxygen species (ROS), and glutathione loss.[84]

![Figure 5. Antimicrobial behavior of graphene materials. Graphene materials can fight against bacteria through various mechanisms such as oxidative stress, hindrance of protein transfer, photothermal interaction, and membrane stress. Reproduced with permission.[184] Copyright 2017, Royal Society of Chemistry.](image-url)
Metal grafted GO\(^{85}\) and protein grafted GO\(^{86}\) have shown to have very effective antibacterial properties. Moreover, graphene derivatives have been reported to be used as antibacterial composite with different metals (Ag, Fe, Cu, Zn etc.), photocatalyst (TiO\(_2\), CdS, MnS\(_2\), etc.), and polymer matrix. Antibacterial activities of graphene derivatives may differ with diverse factors, such as purity\(^{87}\), oxygen functional groups, size (smaller the sheet size, greater the antimicrobial activity)\(^{88}\), layers of graphene and environment\(^{89}\).

Graphene modified antibacterial fabrics show high potential for many varieties of applications\(^{82c,89,90}\) including maternity garments for the prevention of microbial growth on the fabric surface. The graphene modified antimicrobial clothing can be used in hospitals for HCWs, doctors or patients to reduce spread of infectious diseases\(^{90}\). Suitable antimicrobial coatings are not only to be durable and effective on the textile but also harmless for user and environment\(^{90}\). The antimicrobial agent can be introduced in polymer both before extrusion and to the fiber or fabric after extrusion. Other than graphene the following four main types of antimicrobials that can be used on textiles\(^{21c,92}\):

- Metals and metal salts principally silver and copper which deactivates proteins.
- Silyl quaternary ammonium salts, which disrupt the cell membrane.
- N-Halamines which have oxidative properties (biguanides-polyhexamide PHMB).
- Organic molecules (e.g., 2,4,4-trichloro-2-hydroxydiphenyl ether)

### 6.7. Toxicity

It is crucial to know about the toxic effect of graphene in human, animal, and environment as graphene modified materials are likely to increase. They are found to be toxic toward bacteria and some aquatic organisms. On the other hand, graphene has some in vitro applications like cancer treatment, drug delivery, gene transport, and cell culture without significant toxicity\(^{64a,93}\).

### 6.8. Tribological Behavior

Graphene can act as proficient solid lubricant, thus protect from wear. Simple shear capacity, smooth molecular lamellar arrangement plays key role to their self-lubricating property\(^{94}\). Some research has been done on tribological conduct of graphene and demonstrated graphene’s ability in decreasing the wear rate\(^{84b,95}\).

The vision to prepare protective clothing having improved fire-retardancy, abrasion resistance, conductive, homogeneous heat dissipation, antimicrobial activity, higher elasticity and tensile strength, lightweight, water, and wind proof properties may be possible, if textile fabrics are treated with graphene and can be made strongly bonded stable graphene modified textile composites.

### 7. Synthesis of Graphene Derivatives

Graphene functionalization to convert into graphene derivatives is an essential part for the application of graphene. It enhances the reactivity and allows graphene to be used nanofillers in different multifunctional composites. There are many ways of synthesizing GO and rGO.

#### 7.1. Synthesis of GO

Synthesis of GO involves oxidation of graphite by interaction with an oxidant to form graphite oxide. Oxygen containing functional groups become attached to the surface of graphene sheet by oxidation\(^{63a}\). The process generally involves a few steps. Initially graphite is oxidized using an oxidant, such as sulfuric acid. After that, oxidized graphite, is dispersed in water using sonicator, while exfoliation creates graphene oxide. Sonication assist in dispersion of GO sheets separately\(^{96}\). GO sheets remain stable in water due to the oxygen bearing functional groups in its surfaces\(^{97}\). Literatures often inappropriately mix graphite oxide and graphene oxide. Various graphene materials can be differentiated by layer number, dimension and carbon–oxygen ratio (Figure 6)\(^{98}\). Graphite oxide can be synthesized using various stablished methods like, Staudenmaier, Hummer, Hofmann, and Brodie. The methods mainly deal with mechanical and thermal peeling, chemical vapor deposition (CVD)\(^{98a,98b}\), epitaxial growing, etc.\(^{96,99}\) The Hummers method is used widely\(^{96,99}\). Many variations and improvements of these methods are constantly being explored for better results.

Recently a study revealed that alkaline earth metal ions or divalent ions, like Mg\(^{2+}\) and Ca\(^{2+}\) can be applied to modify GO, which enhance mechanical characteristics by crosslinking and forming bond with oxygen containing functional groups\(^{100}\).

#### 7.2. Synthesis of rGO

Distinctive strategies exist for GO reduction to convert it to rGO\(^{101}\). The properties of rGO, the field of application and mechanical properties of composites is largely affected by the reduction methods\(^{63a,102}\). The defects of graphene sheets, which are imparted by oxidation, can be removed and restored by GO reduction\(^{103}\). The three main methodologies that are utilized for GO reduction are chemical method, thermal method, and microwave radiation. Different reducing agents such as hydrazine hydrate, sodium hydrosulfite, dopamine, ascorbic acid, hydroiodic acid, etc., are normally used for chemical reduction\(^{60,101b–d,104}\). In thermal reduction GO is treated with high temperature, where oxygen bearing functional groups breaks and convert to CO\(_2\) and H\(_2\)O\(^{105}\). Sometimes antioxidant is also used to assist thermal reduction\(^{106}\). Microwave irradiation method has likewise been effective\(^{107}\).

Chemicals generally used for reduction of GO are hazardous and harmful. Thermal reduction and microwave irradiation dispense with the require fore chemicals. However high temperatures has some perilous impact on graphene surface, which is a matter of concern\(^{101b}\). More comprehensive study of GO
reduction strategies has been revealed by Pei et al.\textsuperscript{[103]} and Pumera et al.\textsuperscript{[101a]}

8. Fabrication Techniques of Graphene Modified Textile Composites

Graphene derivatives can be widely applied in composites. Owing to economical and high production performance, the majority of graphene modified polymer composites studied are manufactured utilizing GO and rGO as fillers. There are three following primary techniques to incorporate graphene and its derivatives into polymer networks.\textsuperscript{[55e,63a]} The equal dispersion of graphene nanoparticles are the key for the preparation of graphene modified composites.\textsuperscript{[56]}

8.1. In Situ Polymerization

In this method, graphene derivative fillers are let to react with a monomer, sometimes with a suitable catalyst. The polymerization is normally initiated by heat treatment or applying radiation.\textsuperscript{[108]} Due to the robust interconnection between the graphene and the polymer framework homogeneous spreading and excellent miscibility of graphene occurs in this method.\textsuperscript{[109]} Sometimes solvents are used in this method and for solvent removal additional purification steps are required for solvent removal.\textsuperscript{[55e]}

8.2. Solution Mixing

It is most usually utilized method for manufacturing polymer graphene composites among all mentioned methods because of its simplicity, great application potential, and no specialized equipment required. In this method, polymer is solubilized into an appropriate solvent so that graphene can swell. Graphene sheets are needed to be functionalized to reduce solubility and dispersity and aggregation problems in different solvents. Unfortunately, most of the time dispersion of graphene in organic solvent is not stable. Sometimes, particularly with organic solvents, homogeneous mixing is accomplished by means of sonication or shear mixing. This technique ought to be utilized with alert, as reconglomeration of the sheets as a rule happens during solvent evaporation.\textsuperscript{[55e,63a,110]}

8.3. Melt Compounding

In melt intercalation strategy, graphene, and polymer matrix are mixed together in melted condition, implying that dissolvable is not essential in this technique. The uniform mixture is
basically attained by high shear blending at high temperatures. Fabrication of thermoplastic composites is mainly done by this method. The fundamental disadvantages of melt compounding strategy are that the dissipation and conveyance of graphene derivatives in the polymer lattice is very less.\(^{55e,63a,111}\)

Regardless of which technique is utilized, enhancing the dispersion and interfacial bonding between the filler and matrices are crucial difficulties in achieving property upgrades in their composites.\(^{55e,63a}\) GO route (Figure 7) has enormous potential to fabricate graphene composites, minimal effort, cost effectiveness, versatility, and large scale production being the fundamental points of interest.\(^{112}\) However, modification of graphene surface to incorporate suitable functional groups hinders applications and create defects. Albeit a portion of the defects can be minimized by means of reduction.\(^{55e,63a}\) In this way, it is imperative to find new solutions for controlling the extent of introduced functional groups on graphene surface by oxidation with more environmentally acceptable ways and progressively proficient methods for the reduction of GO.

As revealed by many research studies, fabrication of graphene modified protective clothing can be divided into several steps (Figure 8). The first step is “pretreatment of fiber.” To eliminate the contaminants from fibers and enhance the interaction between the fiber surface and graphene derivatives, pretreatment is important.\(^{113}\) For pretreatment generally fiber and fabrics are soaked in acetone or other organic solvent for

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**Figure 7.** The fabrication paths of graphene-modified polymer composites. Reproduced with permission.\(^{55e}\) Copyright 2012, Wiley-VCH Verlag GmbH & Co. KGaA.

**Figure 8.** Schematic flow diagram for the development of multifunctional graphene modified fabrics.
several hours. It is then allowed to ultrasonicate or wash in deionized water and finally, dried in an oven.

Second step is “synthesis of GO.” As discussed earlier in the presence of an oxidant, graphene is oxidized to GO. GO can be synthesized using various established methods like, Staudenmaier, Hummer, Hofmann, and Brodie. These methods deal with mechanical and thermal peeling, CVD, epitaxial growing, etc.  “Preparation of GO solution in water” can be the third step. As oxidized form of graphene, GO show versatile surface chemistry owing to its oxygen bearing polar functionalities (epoxide, carbonyl, carboxyl and hydroxyl groups). Due to the polar groups in its basal pinaacid, GO gets to be hydrophilic in nature, which permits improved interfacial bonding with different fibers. This bonding of GO with fibers improve functional properties. For preparation of GO solution specific amount of GO is mixed with specific volume deionized water. The mixture then allowed to mix thoroughly by magnetic stirrer. After that GO is dispersed in water using sonicator. Sonication assist in dispersion of GO sheets separately. GO sheets remain stable in water due to the functional groups in its surfaces. For further purification the ultrasonicated GO solution is centrifuged.

The fourth step and most important one is “coating” of GO on fabrics. Coating methods and conditions have been modified in many ways based on materials characteristics. Most of the reported research followed facile “immersion and drying” technique. Based on fiber chemistry many modification approach has got attentions for better interaction and bonding between fiber and GO, such as use of adhesives, coupling agents, plasma treatment, chemical activation, grafting via esterification, microwave-assist polymerization (MAP), thiol–ene click chemistry, doping of GO with different metal ions for chemical crosslinking, etc. Moreover, antimicrobial nanoparticles like silver, ammonium salts and TiO$_2$ has also been used with graphene. Fifth step is reduction of GO coated fabrics. GO has some inferior functional properties than pristine graphene due to oxygen functionalization, which can be restored by reduction. GO is transformed into rGO by chemical, thermal, and microwave treatment. The final step is “characterization of modified fabrics and clothing.” Graphene modified fabrics and clothing is normally characterized by different test, such as mechanical properties, electrical properties, thermal/flame resistivity, UV protection ability, antimicrobial activity, self-cleaning behavior, photo activity, moisture absorption, wash fastness, antistatic behavior. Characterization is normally done by standard methods.

9. Graphene Modified Textile Composites in Relevant to the Properties of Protective Clothing

Remarkable progress has been shown on the graphene incorporated and modified multifunctional textile composites by researchers all over the world. This section provides a compilation of research reported in graphene modified different textile/composites in relevant to the properties of smart or protective clothing (Table 2).

Eurojersey and Directa Plus two companies are doing collaborative research to develop new performance graphene modified fabrics. They developed Grafytherm membranes by treating polyurethane (PU)/polytetrafluoroethylene (PTFE) with Directa Plus’s G+ (graphene derivative). Coating of fabrics by Grafytherm provide several performance properties, including bacteriostatic properties, antistatic properties, electrical conductivity, breathability, resistance to shrinkage, waterproofness, windproofness, and flame resistance. Moreover, they help the wearer maintain a comfortable body temperature by facilitating heat dissipation in warm conditions and the homogeneous distribution of heat in cold conditions. Another company, Vollebak, launched a graphene jacket where they combined graphene nanoparticles with polyurethane and then attached with nylon. The graphene modified layer help to equalizing the body temperature.

Hohenstein Institut für Textilinnovation is doing a collaborative research project on using graphene for the surface modification of textiles in heat protective clothing. They are investigating techniques to apply aqueous graphene dispersions (e.g., graphene oxide, multilayer graphene), so that they can be used as a permanent coating on different textile surfaces. Recent research discovered that two layers of graphene stacked on top of one another can temporarily become as hard as diamond when struck by, say, a bullet. This technique could be used for armor and may be used in the development of wear-resistant protective coatings in future.

There is a promising application of graphene coating in body-armor. Researchers of Rice University, Houston, studied on the impact strength, stiffness and elasticity of graphene and found its unique ability to absorb high impact energy of microscopic projectiles. As graphene dissipate stress it can also be used in tanks and armoured vehicles. Using graphene coated nonwoven, recently Changzhou industrial technology research institute of Zhejiang University, China developed graphene antibacterial, antismog mask, which has a PM2.5 filtering efficiency of 96.4%.

9.1. Polyester/Graphene Composites

Polyester is well-known for its excellent thermal, mechanical, and chemical properties that can be processed through almost all the technologies available for textile. The most common polyester used for woven and nonwoven fiber manufacture is polyethylene terephthalate (PET). Graphene and its derivatives can be used for fabrication of PET/Graphene composites. Due to presence of functional groups and better dispersion characteristic GO is favorable. Various techniques were reported for fabrication of PET/Graphene (or Graphene derivatives) composites. Different researchers modified the methods and conditions bases on materials characteristics. Melt compounding, coating via immersion and drying, plasma treatment using bovine serum albumin (BSA), coating using dopamine as adhesive, grafting of polyester onto graphene sheets via esterification, thiol–ene click chemistry under UV radiation, etc. methods are used.

Zhang et al. prepared PET/graphene nanocomposites by melt intercalation technique which show electrically conductivity. By virtue of higher surface area and van der Waals impact, graphene nanosheets can agglomerate. So, it is
Table 2. Research performed on graphene modified fabrics/textile in relevant to the properties of smart or protective clothing.

| Material composition | Method applied | Modified properties/ enhanced properties | Probable application | Reference |
|----------------------|----------------|-------------------------------------------|----------------------|-----------|
| Two layers of Gr on SiC (0001) | Controlled sublimation method: experiments performed on buffer layer, 2L samples grown on SiC (0001) | Stiffness and hardness, which is comparable to diamond | Wear resistance protective coating | [126] |
| Nonwoven fabrics of Gr fibers | GO fibers were fabricated by wet-spinning technique. Nonwoven graphene fabrics prepared by dispersing GO fibers in aqueous solvents and collecting by a mesh. Nonwoven then reduced by both chemically and thermally. | Electrical conductivity and thermal conductivity | Multifunctional fabrics | [187] |
| PET + Gr | Melt compounding (Brabender mixer) and compression molding | Electrical conductivity | Smart PPE | [130a] |
| PET + rGO + polypyrrole | Coating of PET with GO was done immersion and drying followed by chemical reduction. Polypyrrole was coated on fabric by in situ synthesis. The composite was hot pressed to prepare film. | Surface chemistry and wetting behavior | Protective clothing | [130c] |
| PET + rGO | Force penetration of GO into PET by suction filtration and chemical reduction of PET/GO | Electrical conductivity and thermochemical property | Smart clothing | [59b] |
| Polyester + rGO | Coating of rGO onto polyester by plasma treatment and bovine serum albumin as adhesive | Conductivity | Smart clothing | [115a] |
| Polyester + rGO | Coating of nonwoven polyester with liquid crystallite graphene oxide by immersion and drying | Conductivity and thermal activity | Electrically conductive textile | [130d] |
| Polyester + rGO, polyester + Gr, polyester + Gr + Ag | Coating (immersion and drying) and in-situ chemical reduction | Mechanical, electrical and UV protection | High performance textiles | [130b] |
| Polyester + rGO | Grafting of polyester onto Gr via esterification and then chemical reduction | Electrical and thermal conductivity | Smart textile | [110b] |
| PET fabric + rGO | 3-Mercaptopropyltriethoxysilane functionalized rGO applied onto PET fabric under UV radiation for chemical bonding | Moisture absorption, perspiration and thermal conductivity | Sportswear | [121] |
| PET fabric + rGO + TiO$_2$ | GO and AgNO$_3$ were mixed as precursor and dip coating technique used to coat PET fabric. rGO–Ag nanoparticles were coated on fabric by in situ synthesis and chemical reduction using hydrazine. | Conductivity and durability in wash fastness | Smart textiles | [99a] |
| Polyester + rGO + Ag nanoparticles | rGO coatings on polyester fabrics was done by plasma treatment of fabric, using BSA as adhesive and then chemical reduction. TiO$_2$ dispersed on rGO coated fabric by immersion and drying. | Light absorption, conductivity, electroactivity, and photocatalytic properties | Smart textiles | [115b] |
| Polyester + rGO + AgNO$_3$ | GO was introduced to NaOH or ethylenediamine modified polyester fabric. AgNO$_3$ was then added and reduced with GO using ascorbic acid and ammonia to find rGO/Ag nanocomposites coated on fabric. | Electrical resistivity and antibacterial property | New property textile | [188] |
| Nylon 12 + GO | Melt compounding and compression molding | Tensile strength, impact strength, elongation at break, and hardness | Protective clothing | [140a] |
| Nylon 12 + Gr | Dispersed sonicated and centrifuged graphene nanoparticles was coated onto nylon fabric by facile liquid-based immersion at low sonication and low temperature condition followed by drying. | Electrical conductivity | Smart textiles | [189] |
| Nylon-6 + rGO | Bovine serum albumin (BSA) was used as adhesive to wrap GO onto nylon. GO is then reduced chemically. | Electrical conductivity | E-textiles | [133a] |
| Nylon-6 + sulfonated graphene | Using sulfonated graphene (SG) precursor, composite was fabricated by in situ hydrolytic ring-opening polymerization of 3-caprolactam followed by molding | Thermal conductivity and mechanical property. | Thermal conductive systems | [143] |
| Aramid (Kevlar) + GO | Fiber was treated with plasma for surface functionalization. GO sheets was attached to the functionalized fabric chemically using both acidic and alkaline pH conditions. | Tensile strength, shear strength and adhesion property | Advanced high strength composites | [150a] |
| Aramid + dopamine + GO | Due to adhesive nature dopamine was applied on to fiber to form coating of polypyrrole followed by esterification of GO with polypyrrole layer. Reaction temperature and composition were changed to adjust concentrations of new composite. | UV resistance, surface activity, thermal and mechanical property. | High strength fabrics | [150b] |
| Para aramid + graphene + polyurethane | Para-aramid fiber was wrapped by graphene/waterborne polyurethane applying immersion and drying method. Then under different temperature the composite was hot pressed. | Laundering durability | Protective clothing | [152] |
| Aramid (Kevlar) + rGO + dimethylsulfoxide (DMSO) | (DMSO) was used to produce aramid nanofibers (ANF) from aramid fibers. GO reacted with ANF by self-assembly. Composite was obtained by vacuum filtration and then chemical reduction. | Electrical and mechanical properties | Electronic fabrics | [153] |
Table 2. Continued.

| Material compositiona) | Method appliedb) | Modified properties / enhanced properties | Probable application | Reference |
|------------------------|------------------|------------------------------------------|---------------------|-----------|
| Para-aramid + graphene + WPU | Dip coating in graphene/WPU solution followed by hot pressing was used to prepare graphene modified para-aramid fabrics. | Heat resistance and electric heating | Protective clothing | [154] |
| PVA + GO | Gel spinning followed by hot drawing technique used to manufacture GO/PVA nanocomposite fibers. | Tensile strength, antifultra-violet, and antibacterial | Textiles and biomedical | [168a] |
| Cotton + rGO | Immersion and drying method were used to coat cotton fabrics by GO. Composite was reduced by heat in presence of nitrogen. | Electrical conductivity, UV protection and surface hydrophobicity | New performance textile | [61] |
| Cotton + rGO + silane coupling agent | Silane coupling agent was used to increase the bonding attraction between fabric and GO. Coupling agent modified fabric was dipped in GO solution and then dried. GO was reduced chemically using hydrazine hydrate. | Electrical conductivity | Smart textiles | [116] |
| Cotton + GO + TiO₂ (Fe, N-doped) | Dispersed, hydrothermally treated and dried TiO₂+Fe+N+GO applied on to the fabrics by immersion and coating approach | Self-cleaning, antimicrobial and biocompatible | Hospital clothing, sports attires, military uniform etc. | [122a] |
| Cotton + rGO + TiO₂ | Simple immersion and coating were used to coat GO onto cotton. Reduction of GO and nucleation of TiO₂ was done by dipping GO coated fabric in solution mixture of titanium trichloride and poly(vinylpyrrolidone). | Photoactivity efficiency and antimicrobial activity | New performance photoactive, antimicrobial textiles | [122c] |
| Cotton + GO (phosphorus- and nitrogen-doped) | GO was doped with phosphorus and nitrogen using polyphosphoric acid and ammonia solution respectively. The they were used to coat the cotton fabrics. | Flame retardant ability | Flame retardant textile | [75] |
| Cotton + phosphorylated graphene oxides | One-pot technique was applied for phosphorylation of GO (PGO). Cotton/PGO was prepared by immersion and drying technique. Polyethyleneimine electrolyte was used for self-assembly. | Flame retardant ability | Fire retardant textile | [79] |
| Cellulosic/polyamide fabric + rGO | Exhaustion method was used to treat fabrics with GO. Cetyltrimethyl-ammonium bromide use for long time and uniform adsorption of GO. GO-treated fabric was reduced to reduced graphene oxide (rGO) with inorganic and organic reducing agents. | Electroconductivity, antimicrobial activity and UV protection | Multifunctional textile | [156a] |
| Cotton/nylon (cationized) + rGO | For better interaction with GO, nylon was treated with 3-chloro-2-hydroxy propyl trimethyl ammonium chloride for cationization. Fabric was coated by GO through exhaustion method. Composite was reduced chemically. | UV-protection, bioactivity and electro conductivity | Multifunctional textile | [156b] |
| Cotton + rGO | rGO was dispersed in N-methyl-2-Pyrrolidone by ultrasonication. To be coated with rGO, cotton fabric was simply dipped in rGO solution and dried. | Electrical conductivity | Body warmer clothing | [156d] |
| Cotton + Gr/rGO | Cotton fabric was modified by xerogel coatings with Gr and rGO using sol–gel method. Sodium lauryl sulfate was used as anionic surfactant and organosilicon sol was used for padding fabrics. | Antistatic properties | Protective clothes in explosive atmosphere | [156e] |
| Cotton + rGO | Cotton fabric was coated with GO. Reduction of GO and Fe₃O₄ nanocomposite was simultaneously developed on fabric surface by alkaline hydrolysis of magnetite precursors with NaOH. | Electrical resistivity, magnetic properties, antibacterial properties and UV blocking activity | Multifunctional smart textile | [156f] |
| Cotton + GO | The GO was coated onto cotton fiber by simple adsorption, cross-linking via gamma radiation under N₂ environment and chemical crosslinking ammonium persulfate as initiator. | Antibacterial property | Antibacterial textile | [82c] |
| Cotton + rGO + antioxidant | GO was coated on to cotton by simple padding and then immersed in antioxidant solution. GO was reduced by thermal treatment. | Electrical conductivity and hydrophobicity | Smart textile | [106] |
| Cotton + rGO + N-halamine | rGO-polymeric N-halamine was applied on to cotton fabric by immersion and drying technique. The composite was reduced by chemical method using L-ascorbic acid | UV blocking, hydrophobicity, electrical conductivity and antimicrobial activity | Multifunctional antibacterial textile | [190] |
| Silk + rGO | Silk fabric was wrapped by GO through facile dip and dry method. GO coated fabric was then reduced chemically with sodiumhydroxysulfite. | Electrical conductivity, antifultra-violet and water repellent | Medical care textile and E-textile | [158b] |
| Silk + rGO | Coating was done by dip and drying method followed by chemical reduction using l-ascorbic acid | Flame retardant property | Flame retardant textile | [159a] |
| Silk + GO + montmorillonoid | GO hydrosol doped with montmorillonoid and polyvinyl alcohol were coated on silk by coating machine. | Fire retardancy and ultraviolet resistance | Multifunctional flame resistance textile | [158a] |
difficult to accomplish robust interfacial attachment between the composite matrix and graphene. However, polyester can be chemically bonded with graphene nanosheets by modification with different functional groups to form an explicit interconnected assembly.[110b] Adhesives like BSA and dopamine are also found as an effective way to coat fabrics with graphene derivatives. As an amphiphilic polymer of amino acid BSA possess both hydrophobic (nonpolar) and hydrophilic (polar) character, thus can be attached to both organic materials and inorganic materials.[131] Surface charge of BSA largely depends on pH of the solution. It possesses positive charge and negative charge below and above pH 4.9, respectively.[8b] BSA, act like universal adhesive and when adsorbed on to fabrics below pH4.9 has positive charge. They perform by electrostatic self-assembly (Figure 9) to improve the bonding between GO (negative charge) sheets and fabrics (nylon, cotton, polyester, etc.).[132] This approach using BSA can be applied to present textile technologies.\[133a\] Dopamine has also been used as adhesive, which form a polydopamine layer on to the fabrics. Wang et al. prepared Ag/rGO–PET composite fabrics using dopamine and chemical reduction in presence of radiation,[130e] Chemical bonding through thiol–ene click chemistry was used by Zhao et al. to synthesize PET fabric–rGO composite with better thermal conductivity and perspiration. They reported that due to higher thermal conductivity (Figure 10) and moisture absorption the treated fabric composite has huge potential to use in daily and sportswear textile clothing.[121] The figure shows variations within fabric temperature beneath a forward-looking infrared.[121] It is realized from the photographs that the surface temperature of rGO modified fabric elevated with time compared to the untreated fabric, which proves that the treated fabric has better thermal conductivity. Better thermal conductivity of rGO modified fabric enhance sweat evaporate rate, thus become suitable for different application. Besides thermal conductivity, graphene can also show cooling effect through thermal transmission.

Table 2. Continued.

| Material composition | Method applied | Modified properties/enhanced properties | Probable application | Reference |
|----------------------|---------------|----------------------------------------|---------------------|-----------|
| Silk + rGO           | GO was coated onto fabric by dry coating method using a scrubber. GO reduction was done by l-ascorbic acid | Fire retardant and electrical conductivity | Smart textile | [159b] |
| Silk + rGO + BSA or RSF protein | Silk fabric was wrapped with GO by dipping into GO solution. BSA and RSF protein was used as adhesive. It is the reduced thermally. | Electrical conductivity | Smart textiles | [160] |
| Wool + rGO + TiO₂ | Wool was immersed into GO+TiO₂ solutions, where hydrolysis of titanium isopropoxide and chemical conversion by sodium hydrosulfite occurred to form graphene/TiO₂ nanocomposite. Then the composite dried and reduced chemically. | Antimicrobial action and self-cleaning ability | Medical care textiles and smart textile | [122b] |
| Polyester + rGO | For lower surface tension GO was dispersed in N,N-dimethylformamide. Nonwoven polypropylene was soaked into the mixture for coating of GO followed by chemical reduction. | Electrical conductivity | Electronic textile | [166] |
| Calcium alginate + rGO | Sol–gel method was applied for the fabrication of rGO modified Calcium alginate composite. | Thermal stability and carbonization rate | Multifunctional flame retardant textile | [167] |

Abbreviations: Gr, graphene; SiC, silicon carbide; GO, graphene oxide; PET, polyethylene terephthalate; PPE, personal protective equipment; rGO, reduced graphene oxide; BSA, bovine serum albumin; SG, sulfonated graphene; DMSO, dimethyl sulfoxide; ANF, aramid nanofibers; PVA, polyvinyl alcohol; WPU, waterborne polyurethane; PGO, phosphorylation of graphene oxide; UV, ultraviolet; RSF, regenerated silk fibroin.

Figure 9. Interaction between GO and polyester fiber via electrostatic self-assembly of BSA. Reproduced with permission.[135] Copyright 2018, Springer Nature.
The passive cooling in graphene is greater than that of normal cotton fabrics.[72a]

Most of the research show that the polyesters/graphene composites have excellent electrical conductivity to be used as smart textiles. On the other hand, some studies found better thermal conductivity, tensile strength, moisture absorption, and antibacterial activity.

9.2. Polyamide (Nylon and Aramid)/Graphene Composites

Polyamides contain amide bonds C(O)–NH in their core chain. These filaments demonstrate a solid propensity to crystallize, which is additionally reinforced by hydrogen bonds between the oxygen and nitrogen atoms of two various amide groups.[134] Polyamide fibers are prepared by polycondensation of dicarboxylic acids with diamines and ring opening polymerization of lactams (Figure 11).[134]

Polyamides possess good abrasion resistance and mechanical properties which is an important prerequisite for protective clothing, whereas lower thermal stability and sensitivity toward sunlight are the main limitations. Under high temperature conditions, polyamide fabrics have a tendency to oxidative decomposition and yellowing, which can greatly reduce the mechanical and wear properties of the fabrics.[115] The reason for lower thermal stability is, in the presence of oxygen, the hydrogen atom on the polyamide chain forms hydrogen peroxide. Upon exposure to heat, oxidized polyamides form yellow products (azomethine groups), at the expense of the main polyamide chain.[110,116] To solve this problem, some researchers have used antioxidants, metal salts and amines.[117] He et al. reported a mixture of urea, sodium hypophosphite, and adipic dihydrazide as an antidegradation mixture in polyamides. Some chemical agents can also be found in the market which act as antithermal degradation and antiyellowing agents, but polyamide degradation is still being reported.[115b]

Among the polyamide fibers PA 6.6 nylons and aramids, especially Kevlar (poly(para-phenylene terephthalamide)) are the main fibers in terms of applications in textile.[134,138] However, pure amide resin (nylon and aramid) cannot fulfil the requirements and demand. Hence to enhance the properties, polyamide composites modified with nanofillers especially graphene is an area of research need.

9.2.1. Nylon/Graphene Composites

Nylons are thermoplastic polyamide which possess high mechanical strength, brilliant chemical resistivity, and easy
processability.\textsuperscript{139} Nylon 6.6 is in the most widely used polymer in textile. But, because of its solubility in specific solvents and low melt viscosity this polymer is difficult to be treated expansively using solution mixing approach and melt intercalation technique.\textsuperscript{139} However, graphene/nylon composites were found to effectively improve the dimensional stability and thermal conductivity of nylon. Different approaches have been applied to fabricate nylon/graphene composites including melt compounding,\textsuperscript{140} electrostatic self-assembly with BSA,\textsuperscript{133a} microwave-assist polymerization (MAP),\textsuperscript{120} functionalization of graphene oxide (GO) via esterification and solution mixing,\textsuperscript{141} electrochemical method,\textsuperscript{142} and in situ polymerization.\textsuperscript{143}

In most studies of graphene/nylon composites, the projected application was electrical conductivity-based supercapacitors and sensors.\textsuperscript{120,142,144} Nonwoven nylons are normally used for synthesis of conductive fabrics.\textsuperscript{144c} However, some research produced graphene/nylon composites with improved mechanical and thermal properties.\textsuperscript{139,140,143,145} Wang et al. prepared nylon6/sulfonated graphene (SG) composite by a new approach with sulfonated graphene (SG) precursor, through hydrolytic ring-opening polymerization of 3-caprolactam followed by molding. SG layers were dispersed equally within composite matrix, thus the composite showed excellent thermal conductivity (Figure 12) with remarkable mechanical strength.\textsuperscript{143}

Figure 12 depicts the thermal conductivity and normalized thermal conductivity of sulfonated graphene modified nylon 6 polymer. Thermal conductivity of composites was found to have a rapid increase (up to 51%) with the increase of sulfonated graphene and was much higher in comparison to pure nylon 6 polymer. High surface area, equal and wide dispersion of sulfonated graphene and strong interfacial interaction are responsible for that higher thermal conductivity.\textsuperscript{143} This method has shown promise for large scale manufacturing for thermal conductive clothing.

\subsection*{9.2.2. Aramid/Graphene Composites}

As a class of reinforcement fibers aramid fiber possess comprehensive characteristics such as good mechanical strength, toughness, high chemical stability, high heat-resistance, and light weight, which makes these fibers extremely suitable for various applications, including ballistic-rated body armor fabric, protective clothing, marine cordage, etc.\textsuperscript{119,146} Recently graphene modified aramid nanocomposite electrodes for battery and capacitors has gained attention. Most of the literature found on graphene modified aramid composites are for electrical applications.\textsuperscript{147} However, aramid fiber has two intrinsic limitations—the fibers surface is chemically inert (due to high crystallinity)\textsuperscript{148} and poor UV resistance.\textsuperscript{149} Accordingly, their interaction and bonding with materials is poor and surface modification is necessary.\textsuperscript{150}

Surface modification of aramid fabrics can be done by a) plasma treatment,\textsuperscript{117} b) chemical activation,\textsuperscript{118} and c) using coupling agents or grafting.\textsuperscript{119} Zhu et al. shown a novel technique using bilayer wrapping of polydopamine (PDA) and GO to fabricate graphene modified aramid fiber composite having good UV resistivity, enhanced surface activity and thermomechanical properties. Dopamine was used as adhesive and GO coating was done based on esterification and π–π stacking between GO and PDA between GO and polypdopamine.\textsuperscript{150b} Zeng also modified the surface of aramid fibers with polypdopamine for better interfacial attraction with GO. It was found that modification with dopamine effectively enhance the fiber-resin interfacial shear strength and tensile strength (Figure 13) of GO–PDA–aramid composites.\textsuperscript{151}

The laundering durability of a textile composite is important if it is to be used as clothing. Kim and Lee evaluated laundering durability of electroconductive knitted para aramid–graphene–polyurethane composite and found remarkable washing fastness. They concluded that the modified composite fiber can hold its performances up to 10 washing cycles.\textsuperscript{152} In industrial application, Kevlar is usually used as macroscopic fiber, e.g., Kevlar yarns.\textsuperscript{153} Kevlar yarns can be converted to nanofiber to be used in nanocomposites by deprotonation of the amide groups.\textsuperscript{155} Electroconductive para-aramid textile fabrics was fabricated by dip coating in graphene/WPU solution followed by hot pressing. This graphene modified electric heat resistant fabric was successfully tested as protective clothing.\textsuperscript{154}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure12.png}
\caption{Change in a) thermal conductivity (\(\lambda\)) and b) normalized thermal conductivity (\(\lambda/\lambda_o\)) of nylon 6/sulfonated graphene composites with different % of sulfonated graphene. Reproduced with permission.\textsuperscript{143} Copyright 2016, Royal Society of Chemistry.}
\end{figure}
Cotton is the one of the key natural fiber in the textile manufacturing as it possesses characteristic delicate quality, hygroscopic nature and prevalent comfort to skin while wearing. Cotton provides active sites (hydroxyl groups) for functionalization. So, functional modification is a tremendous approach to enhance useful properties and fulfill the expanding needs of customers. Incorporation of graphene into cotton fabric can impart many properties, such as electrical conductivity, flame retardancy, antibacterial ability, self-cleaning, UV protection, mechanical strength, antistatic, etc.

Different techniques have been applied with different materials to fabricate cotton/graphene (or Gr-derivatives) composite. Cai et al. prepared rGO/cotton composite which displayed stable multifunctional activities like conductivity, UV resistance, surface hydrophobicity, etc. Plain weave cotton fabrics surface was coated by GO through a facile immersion and drying method. GO layer on the cotton fabrics were reduced by heat treatment under protection of nitrogen. Same method was also used to fabricate (3-glycidyloxypropyl) trimethoxysilane (coupling agent) modified GO–cotton composite. The silane coupling agent modify the fabric surface by bonding with functional groups in the surface, thus improve the interaction between fabric and graphene derivatives. 

Hasani and Montazer reported using cationic surfactant Such as, cetyltrimethylammonium bromide (CTAB) to prepare stable solution for long-time adsorbing more and uniform GO on cellulose/polyamide fabric. Cationization of cellulose/polyamide (Nylon) by 3-chloro-2-hydroxy propyl trimethyl ammonium chloride was also reported to prepare UV protective, bio-active and electroconductive fabric.

Flame retardance of phosphorus- and nitrogen-doped GO modified cotton fabrics has been reported in some research. Wang et al. reported cotton fabric coated by phosphorus doped GO (PGO) exhibit notable fire retardancy and tensile strength increased dramatically with modification by GO and PDA. Reproduced with permission. Copyright 2018, Springer Nature.
9.4. Silk/Graphene and Wool/Graphene (or Gr-Derivatives) Composites

Both silk and wool has been widely used as high quality textile material. Silk is a natural fiber with good air permeability, hygroscopicity, and superb wearing comfortableness, on the other hand wool is one of the oldest fibers with unique natural properties like softness, warmth, lightness, etc. Silk and wool both are composed of amino acids. Within acidic solution amino groups introduces positive charges. Consequently, electrostatic attraction happens between negatively charged carboxy group of GO and amino group of silk. Thus GO sheets tend to be adsorbed on silk fiber surface. Few researches on graphene modified multifunctional silk and wool fabrics has been reported recently.
Cao and Wang have done a research on surface modification of silk fabrics using simple immersion and drying method with chemically reduced (reduced using sodiumhydrosulfite) GO. After modification the Electrical conductivity, antiultraviolet and water repellent properties significantly increased. BSA and RSF protein were also found to be used as adhesive in silk/graphene composites. Zulan et al. reported highly conductive silk fabric, which was wrapped with GO by dipping into GO.
solution followed by thermal reduction, where BSA and RSF protein was used as adhesive.[160] Flame retardant property can also be improved significantly after several cycles of coating-reduction process.[158a,159] Graphene can also be doped by some minerals, such as montmorillonoid to enhance the fire retardancy and UV resistance.[158c] Graphene modified wool can be used for medical care textiles by imparting antibacterial action and photo catalytic self-cleaning activity.[122b]

9.5. Photocatalytic Fabrics Based on Graphene Derivatives and TiO2 Coatings

Graphene and TiO2 modified multifunctional photocatalytic fabrics have drawn attention due to its electroconductive, self-cleaning, antimicrobial, UV-blocking, and biocompatible properties. These fabrics can be used for healthcare garments, sporting attires, uniform for law enforcement personnel, etc.[122a] Graphene/TiO2 coating on different fabrics is reported recently.[115b,122] Cotton,[122,c,d] wool[122b] polyester,[115b] etc., fabrics are being treated with different manner to coat it by Graphene/TiO2, Fe, N doping, hydrolysis of TiO2, plasma treatment, treatment by BSA, simple dip-dry process, etc., are being applied.[115b,122,161] TiO2 can attach with graphene sheets by several reasons, like free electrons-unpaired π electrons bonding of TiO2 and carbon atoms, electrostatic attachment of Ti4+ with functional groups of GO and hydrogen bonding.[122a]

In the photoactivity mechanism (Figure 18), a UV light source (photon) possessing energy greater than bandgap of TiO2 is allowed to interact with TiO2. Then free electrons come out to the photocatalyst surface. The freed electrons generate reactive oxygen species, ROS (OH−, and O2−), when react with free O2 or water. The ROS damage or degrade and cause toxic effects in organisms.[122a,c,162] However, graphene and its derivatives function as adsorbent, electron-acceptor, and photosensitizer with a large surface area, and efficiently improve photodecomposition and inactivation of contaminants or microorganisms. Thus, photocatalytic process become more effective when TiO2 is modified with graphene.[122c,163] The one limitation is TiO2 nanoparticles demonstrate photocatalytic action only under UV light.[161,164]

9.6. Miscellaneous Composites

9.6.1. Polypropylene/Graphene (or Gr-Derivatives) Composites

Nonwoven polymers like polyethylene are getting significant interest for manufacturing of multifunctional textile. Graphene modified polypropylene showed good property as conductive textile. Three approaches has been reported for conductive polymer fabrication. They are coating, copolymerization and blending. Metallic and carbonaceous are being used as additives to ensure conductivity.[165] Pan et al. prepared GO coated nonwoven polypropylene composite which is has high conductivity and can be used as electronic textiles. The conductive property of the fabricated composite was found stable to washing fastness.[166]

9.6.2. Calcium Alginate/Graphene (or Gr-Derivatives) Composites

As a polysaccharide macromolecule NaAlg can interact with multivalent cations like Ca, thus form crosslinked network and improve their mechanical resistance and barrier properties. Zhao et al. reported preparation of graphene modified calcium alginate composite using sol–gel process. The composite showed improved thermal stability and increased carbon formation, thus showed notable promise as multifunctional smart textiles having good fire retardancy and heat generating ability.[167]

9.6.3. Poly(vinyl alcohol)/Graphene (or Gr-Derivatives) Composites

Poly (vinyl alcohol) (PVA) is a nonhazardous synthetic polymer that has the potential to be applied in producing multifunctional fibers. Incorporation of graphene into its planner zigzag structure can increase its properties remarkably. High hydrophilic nature and hydroxyl group in its structure makes it more suitable to react with graphene.[168] Various methods like electrospinning[168a] gel spinning[168a,c] and wet spinning[169] have been reported to fabricate graphene/poly(vinyl alcohol)
composites. Mechanical strength, electrical conductivity, thermal conductivity, antimicrobial activity, UV protectivity, etc., has been reported to increase when graphene derivatives are added to polyvinyl acetate matrix. Most of the reported composites were flexible and strong to be used in textile. Supercapacitors were also prepared by some researchers to be used in smart textiles.[169]

9.6.4. Graphene (or Gr-Derivatives)/ (Carbon Nanotube, CNT, or Carbon Black)/Fabric Composites

Like graphene, CNT is entirely composed by sp² hybridization. CNT have a length to diameter ratio of about 1 000 000 and possess excellent electrical and mechanical characteristics.[170] CNT/fiber composites have been reported by some researchers. Different chemical modification of CNTs and many methods have been applied to different fabrics such as cotton,[171] Kevlar,[172] polyamide 6,6,[173] polyester,[174] polytetrafluoroethylene, and Nomex fiber.[175] CNTs can impart good electrical conductivity, hydrophobicity, mechanical strength, tribological properties to different fabrics.[174,176] Due to its good electrical conductivity, most CNT/fabric composites show remarkable applicability as smart textiles (conductive textile, capacitors, sensor, and electromagnetic shielding).[170] At the same time, due to its high surface area and high conductivity, carbon black is generally used to enhance conductivity, electromagnetic shield, and strength of composites. Carbon black nanoparticles (CBNP) are comparatively inexpensive and can be easily mixed with polymer matrices.[177] CBNPs have been used with polymers or fabrics like polyethylene terephthalate,[177a,178] polyester,[179] and polyethylene.[180]

However, a very few studies have been done on mixtures of carbon material (graphene/CNT/carbon black) modified fibers. A hybrid of graphene oxide and CNTs was reported to improve the mechanical and tribological behavior of polytetrafluoroethylene/Nomex fiber/phenolic composite.[175] Again, a CNT/carbon black mixture was found to increase electrical conductivity thus increasing electromagnetic shielding properties.[173] Likewise, CNT was added to enhance the conductivity of nonwoven fabric/rGO composite and cotton/graphene.[181] Most of the studies of CNT and CBNP were conducted with graphene derivatives to increase the electrical conductivity. Further investigation could be done on Graphene (or Gr-derivatives)/(carbon nanotube or carbon black)/fabric composites.

10. Strength and Challenges for Using Graphene in Modifying Protective Clothing

Alongside the benefits and strength, using graphene in PPE clothing has some limitations and challenges too. A summary of the strength and challenges of the use of graphene for PPE clothing is shown in Table 3.

11. Conclusions and Perspective

Multifunctional protective clothing has gained attention due to increasing potential health hazards, multihazard environments, and concern for work health safety. Despite some remarkable innovations in the field of protective clothing, there remain many limitations, challenges, and areas to improve. Heavy weight, bulky nature, lack of mobility, heat stress, low heat dissipation, physical stress, lack of breathability, lower protection against pathogens and hazards, lack of protection against chemical, and mechanical hazards are some of the limitations of various current PPE.[1] New research in protective clothing is essential to overcome these shortcomings.

Graphene modification of polymers/textiles can be a potential approach in this regard. All the unique properties of graphene such as, mechanical strength, flame-resistant abilities, conductivity, antibacterial activity, resistance to abrasion, and UV-protectivity can be unified with properties of protective clothing in one lightweight application if textile fabrics could be modified with graphene/graphene derivatives in an effective way.[8] In spite of the outstanding properties of graphene and its derivatives, graphene modified fabrics (nylon, cotton, polyester, etc.) are not yet adoptable for large scale textile

Table 3. Strength and challenges of using graphene to modify personal protective clothing.

| Strength | Challenges | Solutions |
|----------|------------|-----------|
| • Graphene and its derivatives have unique properties (Mechanical, thermal, electrical antibacterial, chemical, UV blocking etc.), which are essential in terms of PPE clothing.[65] | • Difficulties in dispersion and interfacial interactions between textile and graphene to ensure stability and sustainability.[51,63] | • Modification and functionalization of graphene and fiber surface for their better interfacial interaction and chemical bonding using different modifiers. |
| • Oxygen bearing functional groups (epoxide, carbonyl, carboxyl and hydroxyl groups) in GO, permits improved surface interaction and bonding with polar polymer matrices.[51,53,57] | • Sometimes inferior physical properties of graphene derivatives in composites than perfect graphene | • Use of coupling agents, alkaline hydrolysis of fibers. |
| • Hydrophilicity and dispersion ability of GO in different polymer matrices.[57,59] | • Aggregation problems of graphene sheets owing to not only large surface area but also van der Waals force[110] | • Allowing electrostatic interaction using plasma treatment or amphiphilic adhesive. |
| • rGO minimize application hindrance, reduce the defects and bring properties close to pristine graphene.[51,63] | • Lack of viable high-quality large-scale production method and chemical stability | • Using metal ions as crosslinking agents. |
| • Graphene has shown its compatibility to be used with various fabrics (Polyester, polyamide, cotton, silk, etc.) and different methods. | | • Applying thiol–ene chemistry, grafting using esterification. |
manufacturing.\[^{13a}\] Comfort and sustainability is an interesting issue for graphene modified clothing. As graphene is a monoatomic thick nanomaterial, it is expected that, it will not cause major discomfort. Moreover, has desired multifunctional properties which can reduce the discomfort of conventional protective clothing. To ensure sustainability and good stability of graphene coated protective clothing, modification, and functionalization of graphene and fiber surface is essential for their better interfacial interaction and chemical bonding. More research should be done to address sustainability.\[^{55e,63a}\] Other challenges of graphene modified textile clothing, which hinder its application are lack of viable high-quality large-scale production method, less interaction of carbon with chemicals and low dispersity of graphene in solvents.\[^{63b}\]

Recently notable progress has been revealed on the graphene modified multifunctional textile composites by scientists all over the world. Protective clothing cannot guard against all hazards. Working environment, type of associated hazards, duration of exposure, atmospheric conditions, and many other factors determine the selection of appropriate protective clothing.\[^{38a}\] Different fibers such as, polyester, cotton, and polyamide have been reported to be modified by graphene using different techniques and materials. Modified composite fabrics show promise as protective clothing. Graphene functionalization and GO reduction are the promising ways to improve the processabilities and for obtaining bulk graphene respectively. Reduction of GO is considered an effective way to manufacture graphene-based textile composites for GO’s versatile surface chemistry.\[^{63a,110b,114}\] By combining different textile fabrics with graphene or graphene derivatives, different protective clothing with desired properties can be prepared. More research must be done for the further progresses in this promising field. This review lays the groundwork for future research on graphene modified multifunctional fabrics for PPE.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

graphene, protective clothing, textiles, graphene/polymer composites

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