Review Article

Katarzyna Kośla*, Magdalena Olejnik, and Karolina Olszewska

Preparation and properties of composite materials containing graphene structures and their applicability in personal protective equipment: A Review

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Abstract: Graphene is a new, advanced material with many possible applications in basic and clinical medicine, electronics and automation. Graphene compounds can be successfully used as an integral part of drug delivery systems, in the construction of transistors, polar processors, touch screens, solar cells and in the production of materials for the manufacture of personal protective equipment, *i.e.* products and equipment intended to protect the health and life of users. The literature review presented in this paper concerns physical and mechanical properties of composites containing graphene or its structure as well as methods of obtaining polymer, metallic and ceramic composites doped with graphene structures. Data analysis of the potential use of graphene and its composites in personal protective equipment such as monitoring sensors, clothing and security equipment such as ballistic armor, helmets and protective clothing were also reviewed and summarized.

Keywords: graphene, composites, personal protective equipment, graphene composites preparation, graphene composites properties

1 Introduction

In order to systematize the latest literature reports on the use of graphene in composite materials, the knowledge on the properties of composite materials containing graphene

structures, *i.e.* linear and flat textiles, ceramic, metallic and polymer composites and their use in personal protective equipment applications has been reviewed.

Research on graphene obtainment has been conducted for about 40 years. Until recently, however, they did not produce satisfactory results. Only after 2004, a group of scientists headed by Geim and Novoselov [1] managed to isolate graphene, for which in 2010, the scientists received the Nobel Prize for Physics. For many years now, graphene has been of interest to research teams around the world, including scientists dealing with composite materials in the broadest sense of the term.

Graphene is an allotropic variety of carbon in the form of a single, two-dimensional atomic layer. Carbon atom orbital bodies occur in the hybridization of sp^2 and form six-atom rings arranged in a grid in the shape of a "honeycomb".

Graphene is characterized by a significant Young's modulus of about 1 TPa, high mechanical resistance, high tensile strength (about 130 ± 10 GPa) and elasticity (graphene can be stretched up to 20%). Furthermore, it shows a low resistance value of $10^{-6} \Omega \times \text{cm}$ (at the temperature of 300 K), significant mobility of charge carriers at room temperature (about $2 \times 10^5 \text{ cm}^2/\text{V} \times \text{s}$) and also significant density of charge carriers ($> 10^{12} \text{ cm}^{-2}$) and thermal conductivity (reported value $> 5000 \text{ W/m} \times \text{K}$ is questioned in some studies indicating rather 1500–2000 $\text{W/m} \times \text{K}$). Furthermore, deposition of a single layer on an amorphous substrate reduces conductivity to 500–600 $\text{W/m} \times \text{K}$ [2, 3]. However, most of these features cannot be achieved in practice. Theoretically modeled physicochemical parameters of graphene plane are modified by impurities, defects, admixtures, presence of substrate, connection of several layers or chemical functionalization.

In view of the above facts and the fact that the exact numerical values for characterizing graphene and its derivatives depend to a large extent on the method of preparation, methods of graphene purification, its functionalization or measurement conditions, the data presented

*Corresponding Author: Katarzyna Kośla: Institute of Security Technologies „MORATEX”, M. Skłodowskiej-Curie 3, Street, 90-505 Lodz, Poland; Email: kkosla@moratex.eu

Magdalena Olejnik, Karolina Olszewska: Institute of Security Technologies „MORATEX”, M. Skłodowskiej-Curie 3, Street, 90-505 Lodz, Poland

above describing the physical and mechanical properties of graphene should be treated as approximate and indicative.

Graphene as a nanomaterial can be obtained by top-down, *i.e.* miniaturization of existing systems, or bottom-up, *i.e.* aggregation of atomic-molecular individuals into structures of nanometric dimension. In connection with the above, we can distinguish methods consisting in the grinding of graphite classified as top-down and regrouping/condensation of carbon atoms classified as bottom-up. The main top-down and bottom-up graphene production techniques are: dry graphite delamination [4, 5], liquid phase delamination [6, 7], growth on silicon carbide [8], chemical gas phase deposition (CVD) [9–12], epitaxial methods [13], thermal conversion of amorphous carbon and other carbon precursors [14], chemical synthesis [15–18].

In most cases, the methods of graphene preparation described above lead to the formation of single- or multi-layer graphene with a significant number of defects and functional groups. Such products have far from theoretical physicochemical properties, but this does not necessarily disqualify them, when they are used, *e.g.* as a composite. The characteristics, structure and quality of graphene used in the manufacture of composites need not necessarily be identical to those of graphene used in the construction of high-precision electronic circuits, so that the different production methods may be useful for the production of a material that can only be used for a distinct group of applications.

In the framework of this work, the literature data were reviewed in order to verify the applicability of graphene and its derivatives, such as graphene oxide in the manufacture of personal protective equipment and to determine the effect of graphene on the physical and mechanical properties of composites and the protective properties of the products and equipment intended to protect the health and life of users.

A compilation of the latest knowledge in terms of properties of linear and flat textile products modified by graphene is a novelty element of this literature review. The properties and possibilities of using composites containing graphene or its structures, *i.e.* graphene oxide or reduced graphene oxide in personal protective equipment, was presented for the first time in this article.

2 Preparation of composites containing graphene

2.1 Preparation of polymeric warp composites containing graphene

The production of polymeric composites with graphene addition is carried out by several methods, including in situ polymerization, melt mixing and solvent method [19–22]. The choice of the composite production method depends on the type of warp, mainly polarity, polymer molecular weight, polymer functional groups and graphene functionalization method [23, 24]. The simplest method of obtaining a composite is the solvent method. However, it is only used for polymers that are dissolved in standard solvents (water, DMF, acetone) and are stable in this state. The composite is formed in several stages, including the dispersion of graphene in a suitable solvent, incorporation of molten polymer into the mixture and evaporation of the solvent. The most important role is played by the solvent in the process, which should be selected so that it does not degrade the polymer, ensures its dissolution, ensures good graphene dispersion and is easily removable from the system. This method was most frequently used for the production of composites based on epoxy resins, poly(vinyl alcohol), polyethylene, polyacrylonitrile, poly(methyl methacrylate). The limitation of the method is the necessity to use environmentally harmful solvents [25].

The second most popular method of manufacturing polymeric composites with graphene filler is the method of mixing components in molten state. It is considered to be much more environmentally friendly and more cost-effective than the solvent method. The method does not use any solvents and the polymer with graphene is mixed at increased temperatures under shear stress. The method of mixing components in the molten state is used mainly for thermoplastic composites. The disadvantage of the method is a lower degree of graphene dispersion than in the solvent method. It is troublesome especially with high graphene content in the composite due to increased viscosity of the system. The in situ polymerization method consists in mixing graphene with monomer, which is then polymerized and binds the graphene pieces into its structure. This method is used for the production of epoxy, styrene and polyurethane warp composites [26, 27]. The advantages of in situ polymerization are the high homogeneity of graphene particle dispersion. The disadvantage, similarly to the method of mixing the components in the molten state, is a rapid increase in viscosity, especially dur-

Figure 1: TEM micrographics of nanocomposites: PE/2,8%Graphite (a, b), PE/5,6%Graphite (c) [32].

ing the production of composites with high graphene content [28].

With the use of solvent-based and melt mixing methods, polymeric composites, *i.e.* polyolefin or low-density chain polyethylene with about 5% mass graphene content were obtained [29, 30]. The solvent-based method gives better results than the alloy-based mixing method. Moreover, the presence of graphene improved the surface conductivity and mechanical properties of the composites. For the content of 5% graphene supplement by mass, the surface conductivity increased by several orders of magnitude. Moreover, this method was used to obtain polyvinyl chloride doped with graphene, which provides reinforcement, thermal stability and conductive properties of polyvinyl chloride (the maximum conductivity value was 0.058 S/cm at 6.47% volume of graphene) [31]. On the other hand, the *in situ* method was used to obtain exfoliated polyethylene nanocomposites (Figure 1) [32] and poly(methyl methacrylate) [33].

2.2 Preparation of ceramic matrix composites

The most popular methods of manufacturing and synthesis of ceramic materials include: free sintering in air, vacuum or protective atmospheres, pressure sintering (HP and HIP), plasma electric spark sintering, selective laser beam sintering.

The method of sintering powders allows to mix with each other materials with significant differences in density, often these are non-reactive materials, in which the connection between the matrix and the admixture phase is mechanical. Preparation of ceramic composites with graphene addition is usually carried out using free sintering and Spark Plasma Sintering (SPS) methods [34–37].

Free sintering (pressure sintering) results in a porous sintered material with suboptimal properties. Sintering under pressure consists of simultaneous interaction with the molded part, temperature and pressure. External pressure influences the sintering mechanisms: it facilitates the regrouping of grains, activates the phenomena of diffusion flow and eliminates pores in the final stage of sintering. Mass transport processes are intensified so that the process can be carried out in shorter times and at lower temperatures compared to free sintering. To extend the life of the dies, the pressing process is carried out in an argon protective atmosphere and the walls of the dies and punches are coated with a lubricant, *e.g.* boron nitride (BN), which prevents the molded part from sticking to the die. Another form of free sintering is the hot pressing method, called HIP (Hot Isostating Pressing - isostatic forming with simultaneous sintering). The HIP method makes it possible to obtain products with complex shapes from almost all known powders. The sinters obtained are characterized by a small number of pores and, consequently, high mechanical properties. Sinters made of “*nano*” powders have lower sintering temperatures than traditional materials. The activation energy is also lower, so that the sintering process of nanomaterials is faster and the full density of the material is obtained at lower temperatures in comparison to polycrystalline materials. This method was used to obtain, among others, $\text{Al}_2\text{O}_3\text{-ZrO}_2$ [38], Si_3N_4 [39] or $\text{Cu/Ti}_3\text{SiC}_2/\text{C}$ [40] composites with graphene.

SPS sintering is one of the most modern powder sintering methods. The characteristic feature of this method is the use of impulse current to heat sintered materials. This method enables sintering of a wide range of powder materials, from nano-scale to micro-powders of metals, ceramics, intermetallic compounds and composite powders. The SPS method was used to obtain silicon carbide and graphene-doped alumina oxide [41, 42].

2.3 Preparation of metallic composites

The manufacture of metallic composites with added graphene is carried out, *inter alia*, by means of the following methods: chemical vapor deposition (CVD), powder methods, electrochemical processing, layer-by-layer processing or liquid metal infiltration [43–48]. The CVD method is used to obtain graphene metallic nanocomposites based on copper (Figure 2) or nickel (Figure 3).

A detailed review of the methods of preparation and properties of copper/graphene composites was presented by Hidalgo-Manrique *et al.* [50]. Obtaining metallic nanocomposites is carried out by depositing single layers of graphene on a copper or nickel substrate in a high-temperature reaction chamber. It is also possible to obtain

multilayer structures by subsequent deposition of single layers of graphene and metals on a given surface.

The epitaxial method is used to produce carbon structures in the form of single and/or multilayer graphene on the surface of copper and/or copper alloy powders. It consists in heating in a fluidized state at temperatures higher than or equal to 750°C copper or alloy powders containing more than 80% of copper with grain sizes from 1 nm to 1 mm. The heating is carried out in a chemically active working atmosphere containing an inert shielding gas and/or a gas reducing pollution and a gas being the precursor of carbon in the pressure range of 20 mbar - 2 bar. In the current research using this method it was possible to obtain copper powders coated with graphene in amounts up to 100 g in one process (about 1.0-1.5 m² surface).

Figure 2: Surface morphology of electrodeposited Cu and Cu-GO coatings [47].

Figure 3: SEM image of the N-CNTs/N-graphene hybrid grown on the surface of nickel foam (a); the top view of low and high magnification SEM images of the N-CNTs (b, c); low-magnification and high-magnification SEM images of one side view of N-CNTs and N-graphene on the surface of the nickel foam (d, e); SEM image of the only N-graphene layers grown on the surface (f) [49].

3 Properties of selected composite materials with addition of graphene

3.1 Polymeric composites

The extraordinary interest in graphene and its properties has led to a lot of research into new applications of this material. It is used, among others, in the production of electronic and optoelectronic devices or as a nanofiller in polymeric composites [51]. The graphene additive improves the properties of the polymeric materials in the composite, but the compatibility between the individual components of the composite is decisive.

In the case of polymeric composite materials containing graphene as a nanofiller, both the graphene distribution and the interaction between the phases of the composite material influence the improvement of physicochemical properties of the material. The trend of the tests is to obtain composites with homogeneous structure. Depending on the polymer used and its properties, when combined with graphene, two groups can be distinguished: polar and non-polar polymers. Examples of polar polymers are polycarbonates, methyl polymethacrylate or naphthalene polyoxide. When graphene is used as a nanofiller for

polar polymers, its dispersion is facilitated by the presence of thermally reduced graphene oxide and unreduced oxygen groups on the surface. These groups facilitate the interaction with polymers of polar character, which leads to obtaining composites with new physical-mechanical properties, such as, *i.e.* increased stiffness [30, 52]. In case of non-polar polymers such as polyethylene, polypropylene or polystyrene, however, there is often a problem with proper connection of the polymer with polar graphene particles and its derivatives. Obtaining a homogeneous mixture becomes more difficult, so in order to obtain a better affinity, vaccination reactions based on the attachment of functional groups, *e.g.* maleic anhydride to the polyolefin chain, are carried out [53].

As the analysis of literature data has shown, graphene addition often causes the polymeric composite to show completely new properties, which include: thermal, mechanical, barrier and electrical properties [54–56]. It has been shown in the literature that dispersed graphene flakes in the amount less than 3% of mass significantly improve the properties of polymeric matrices [7, 52]. The improvement of physical-mechanical properties of composites in the presence of graphene additives or its derivatives in polymers such as: methyl polymethacrylate - PMMA [57–59], polystyrene - PS [60–63] or polyvinyl alcohol - PVA [4, 64, 65] can be considered as an example. Moreover,

polymer composites with added graphene may have new physicochemical properties or contribute to the improvement of polymeric materials properties, *i.e.* mechanical properties or flammability.

The studies also showed that graphene addition improves anti-aging properties [66–68], and in the case of polar polymers (*e.g.* PMMA) it results in obtaining a composite with increased stiffness [52].

Polyurethane nanocomposites are a relatively common group of materials with graphene addition [69, 70]. Example of SEM images of thermoplastic polyurethane (TPU) powders and reduced graphene oxide (RGO) coated TPU powders with 0, 0.5, 1.5, 2.5, 3.5 and 4.5 wt% RGO were shown in Figure 4.

As the literature shows, these materials are subject to constant modifications, including the use of thermally reduced graphene oxide. So far, studies have been conducted in which solid polyurethane elastomers as well as microporous and foamed elastic and viscoelastic polyurethane foams have been modified. These studies showed that after graphene oxide modification, polyurethane nanocomposites are characterized by higher mechanical strength, showing about 30% higher stress at tear up, while the recorded strain decreases with increasing amount of nanofiller. The studies also showed

higher thermal stability compared to unmodified systems [71]. Other research performed by Piszczuk *e.g.* [72–74], allowed to develop polyurethane nanocomposites containing reduced graphene oxide. Thanks to the work carried out, it was possible to obtain more durable materials, *e.g.* for the production of sole elements, shoes or insoles. The essence of the presented invention was the application of reduced graphene oxide in polyurethane matrices [72–74], which positively influences the improvement of a number of functional parameters of modified systems. Polyurethane, which contains reduced graphene oxide, has increased abrasion resistance while maintaining the elastic properties typical of elastomers. This material has dissipative properties that prevent accumulation of electric charge on its surface and has unique mechanical and thermal properties (higher thermal stability of modified systems). In addition to long-lasting footwear, this material can also be used for abrasion-resistant components such as sealing rings and gaskets. In addition, the developed polyurethane nanocomposites with the addition of reduced graphene oxide have a number of other potential applications. These materials are characterized by higher resistance to abrasion or multiple bending and aging. Thanks to these features, they can also be used to produce shock absorbers, spring elements, anti-vibration elements

Figure 4: SEM images TPU powders and of reduced graphene oxide-coated TPU powders. (a)–(g) respectively refer to the RGO content of 0, 0.5, 1.5, 2.5, 3.5 and 4.5 wt% [70].

or noise reducing elements. Recent studies have also observed beneficial bacteriostatic properties of this material using reduced graphene oxide in the polyurethane material.

Another large group of polymers with added graphene or its structures under investigation are polydimethylsiloxanes (PDMS) [75–77]. An example of such a polymer is a composite containing a polymethylsiloxane and a three-dimensional graphene in the form of an aerogel. This composite was obtained by impregnation of PDMS with graphene assisted by vacuum hardening process. Due to the combination of the structures of three-dimensional graphene and polymer, the composite is characterized by high values of compressive strain (at the level of 80%) and tensile strain (at the level of 90%). In addition, it has a high electrical conductivity of 1 S/cm and a thermal conductivity of 0.68 W/(m×K), a stable piezo resistive effect, a fast electrical effect (according to Joule's $(dT/dt)_{max} > 3 > C/s$ during heating 12 W/cm³), high water repellency (wetting angle 135°). The composite also shows a negative temperature coefficient of expansion with reduced electrical resistance over a wide temperature range, exhibiting semiconductor-specific behavior and a double two-dimensional / three-dimensional network causing changes of the conduction mechanism [78].

Other studies carried out on the modification of the properties of composites containing polydimethylsiloxane, natural and butadiene-styrene rubber and graphene in the form of functionalized graphene flakes in their

structure were conducted by Ozbas *et al.* [79]. The results obtained allowed to determine that the composites with graphene addition showed significant improvement of mechanical properties related to the presence of graphene flakes. For the composite containing 1% by weight of graphene flakes, the obtained stress-strain curves showed a modulus increase of 150%, whereas for the composite containing 2% by weight of graphene flakes the modulus increase of 400% was observed [79].

It was also determined that in case of PDMS composite doped with graphene foam (GF) and carbon fibers (CF) (Figure 5) the tensile strength increases by 52% and Young's modulus by 71% in comparison to graphene-free and carbon fiber-free composite. Moreover, for the composite in question the thermal conductivity was 0.55 W/m×K, which means an increase of about 162% in comparison to the unmodified polydimethylsiloxane [80].

Other studies have shown that such composite materials based on polysiloxy acids and graphene have a high absorption efficiency of electromagnetic waves. Composites with 3% graphene by weight show an effective absorption of electromagnetic waves of about 69 dB, which in comparison with composites without graphene (10 dB) results in an increase of absorption properties of 80% [81].

Other examples of polymeric composite systems containing graphene and its derivatives in their structures are epoxy materials. The properties of this type of materials have become the subject of numerous research studies due to the growing interest in epoxy materials in aviation. Addi-

Figure 5: SEM images of freeze-fractured surfaces of (a) GF/PDMS composite, (b) 2 wt%, (c) 4 wt%, (d) 6 wt%, (e) 8 wt%, (f) 10 wt% CF/GF/PDMS composites [80].

tion of graphene to epoxy resins may lead to improvement of strength properties of the material, change of permeability for gases, as well as increase in chemical and thermal structure - features desirable in aircraft structures [28].

Existing works concerning graphene reinforcement of carbon-epoxy composites focus mainly on doping the polymeric matrix of the composite with graphene flakes of small (nanometric) dimensions and strength studies of such composites. Such investigations were carried out, among others, on a composite made of modified graphene flakes of epoxy matrix with carbon fibers. The increase of compressive strength of graphene composite by over 40% in comparison with graphene-free resin was shown. In addition, the coefficient of transverse elasticity of the material increased from 7% to 15% depending on the graphene content of the resin (3% and 5% respectively). There are also reports on the basis of which graphene addition was determined at the level of $0.25 \pm 1.5\%$ mass and a decrease in tensile strength of the material with an increase in graphene content was observed. Composites with 0.25% graphene addition showed 25% higher tensile strength than composites without graphene. However, when graphene content was higher than 1% by weight, graphene composites had worse properties than composites made of resins without graphene. Similar trends continued in the bending strength tests. In this case, only composites containing no more than 0.5% of graphene showed a 9% higher flexural strength than standard carbon-epoxy composites. The authors conclude that the decrease of strength properties together with the increase of graphene content in the composite is caused by the difficulty of homogeneous graphene dispersion in the resin with high mass participation of graphene. In addition, high graphene content increases the viscosity of the resin, which results in the formation of cavities in the structure of the composite, which adversely affect its properties.

Another way to improve the properties of epoxy-carbon composites is to use graphene as an envelope of carbon fibers (*so called sizing*). In the works [82, 83] it was proved that this way the adhesion between the matrix and the reinforcement can be improved, which significantly increases the strength properties of the composite. An improvement in adhesion between composite components by about 11% has been proved. The authors claim that the improvement in adhesion may be due to two reasons. The first is the occurrence of a reaction between the graphene and the matrix, thanks to which additional hydrogen bonds are formed. The second reason results from easier wettability of fibers covered with graphene sizing by the resin. Addition of graphene to carbon-epoxy composites may reduce the appearance of delamination and

cracks, especially those occurring at the moment of damage caused by impact. Mannov *et al.* [84] investigated the influence of the use of thermally reduced graphene oxide on the properties of carbon-epoxide preregs. It was estimated that graphene addition increased residual compression strength after impact. This is due to the increased resistance of the material to delamination and cracks already at 0.5% graphene. It has been noticed that composites reinforced with graphene have a lot of defects and emptiness. This is due to the way in which such materials are produced, which consists in impregnating the fibers with a polymeric matrix doped with graphene. Too much graphene results in an increase in polymer viscosity and thus in a more difficult impregnation of the fiber and contributes to the presence of gaps in the final composite. It was observed that these gaps decrease the residual strength of the composite, which reduces the positive effect of graphene addition. However, the increase in residual compressive strength was estimated to be higher by 19% for graphene samples than for those without graphene. Qin and co-workers [85] presented a different way of preparing preregs. It assumes that the carbon fibers are coated with a thin layer of graphene resin, then impregnated with resin and formed into a prepreg. The preregs were then used to produce a unidirectional composite using the autoclave method. It was observed that the bending strength in the “90” direction of composites with graphene-covered fibers is 30% higher than that of fibers with sizing made of resin only. No significant differences were observed for the direction 0 (increase by 7%). An increase in shear strength by 19% was observed for composites with graphene. Electrical conductivity was also studied, where an increase in conductivity of 162% for fiber/graphene/resin in comparison to fiber/resin composites was noted.

In addition to its mechanical properties, graphene in carbon-epoxy composites contributes to a better thermal resistance of the material, therefore graphene coatings can be used as an ignition reducing element in composites. Epoxy resin has a very low thermal conductivity. The conductivity of a material with 5% graphene added by mass is 4 times greater than that of a material without graphene. The increase of graphene content in the composite to 20% contributes to the increase of thermal conductivity from 1 W/m $\times$ K (for 5% graphene content) to 6.5 W/m $\times$ K (for 20% graphene content).

Studies carried out by other authors concerning thermal conductivity of nanocomposites composed of functionalized graphene and epoxy showed that such nanocomposites have higher thermal conductivity by 10% compared to pure functionalized graphene, but

also proved that functionalized graphene introduced into the composite has much lower conductivity than pure graphene [86].

3.2 Ceramic composites

Ceramics is a material characterized by high resistance to corrosion or abrasion. In addition, it is a good insulator for both electrical and thermal insulation. However, it is fragile and sometimes not strong enough. The fragility of ceramic materials is usually not a desirable feature, and therefore this property has been tried to eliminate as much as possible. This effect can be achieved by the introduction of dispersion reinforcement, which is more ductile or prevents the development of cracks.

Graphene and graphene flakes began to be used to strengthen corundum ceramics [87, 88]. As shown in the studies, the addition of graphene in the form of about 0.8% vol. allowed to increase the resistance to fragile cracking of Al_2O_3 by about 40%, compared to the addition-free corundum ceramics [89]. Moreover, Liu and co-workers determined that for the composite Al_2O_3 containing 0.38% vol. graphene in the form of graphene plates of 6–8 nm size, the increase of fragile fracture resistance was about 27% ($4.49 \pm 0.33 \text{ MPa} \times \text{m}^{1/2}$), the increase of bending strength at the level of 31% ($523 \pm 30 \text{ MPa}$) was also observed. Graphene flakes located between grains of Al_2O_3 (Figure 6) acted in two ways, improving the properties of resistance to fragile cracking. They branched out the propagating crack or formed bridges, grafting the resulting crack planes. The porosity of the obtained ceramics increased with a further increase of graphene in relation to

Figure 6: SEM images of fracture surfaces of the sintered samples. (a) is the sample without GPLs. (b) and (c) are the samples with GPLs. The arrows indicate GPLs embedded in the matrix [90].

Al_2O_3 , which resulted in a decrease in bending and cracking strength resulting from the presence of pores acting as crack initiators. These composites were obtained using the Spark Plasma Sintering (SPS) method [90].

The SPS process can be successfully used in the production of silicon carbide ceramics. It should be noted, however, that it allows to obtain small samples and thus currently remains only a laboratory method. SPS method was used to prepare SiC samples of granulated SiC containing graphene and silicon carbide with graphene added in the form of powder. The first mixture was characterized by higher hardness, and the highest hardness value was recorded for 2.5% strengthening of graphene oxide. A higher thermal diffusivity of samples made of powdered silicon carbide [91] was also demonstrated.

SiC ceramics with different graphene content can also be obtained by pressureless sintering of the solid phase. Research has shown that this method significantly increases the resistance to fragile cracking. Resistance to fragile cracking increases with increasing graphene content, due to better graphene properties, as well as the hardening mechanism of deformed graphene layers, cracked surface areas, moving between graphene layers, increasing the number of cracks and reducing their ramifications, which can dissipate some of the cracking energy. On the basis of the conducted research it was found that in the case of 2% by weight or more of graphene, the strength of silicon carbide samples increased significantly. The effect of graphene addition, apart from the increase in resistance to cracking, is also an increase in bending strength and hardness [92].

In addition, a number of studies were carried out on the application of graphene admixtures to ceramics made of silicon nitride [93, 94]. This type of ceramics was obtained by homogenization in a rotary-vortex mill in an isopropyl alcohol environment, followed by hot pressing at a pressure of 25 MPa at 1750°C for 60 minutes in an argon atmosphere. On their basis it was determined that the introduction of large amounts (above 4%) of graphene into the matrix of silicon nitride causes deterioration of mechanical properties of the sinters obtained. During the measurement of the specific resistance of ceramics with 0.5% graphene content, the upper limit of measurement capability is reached. Increasing graphene content in the composite causes a decrease in resistance value depending on the amount of additive. Moreover, it was determined that the electrical resistance with a large amount of additive decreases the value with an increase in temperature [93, 94].

Borzęcki [95] showed that with the increase of graphene content to 3% by weight, a change in the shape of graphene flakes is visible. The value of the shape fac-

tor $\alpha = 2.6$ in composites with low content (1% by weight of graphene) proved their elongated shape. The increase in the share of flakes to 2-3% by weight resulted in a decrease in the α coefficient and an increase in the average "thickness" of the flake (d_{min}), while it did not significantly change the average diameter of the equivalent flake d_2 , whose value is similar for all graphene contents and amounts to approx. 7 μm . Analyzing the presented results it was found that an increased share of flakes leads to disturbances in the homogenization process, the direct consequence of which is a change in the morphology of flakes used to strengthen the composite by their "curling" and/or agglomeration in the mixing process.

Density and porosity measurements show that graphene addition in the ceramic composite decreased the density of the composite in comparison to the original material. The highest relative density of 96.5% was observed for the composite 1% weight graphene, then with the increase to 3% weight graphene, the density of the composite decreased to 94.1%. The presence of flakes, and in particular the change in their morphology, leads to the generation of a certain number of pores/granules in the structure of the composite, which may cause the decrease in the strength properties of the material. On the basis of the obtained research results it was stated that with the applied consolidation methods and the obtained degree of dispersion, the weight share of flakes exceeding 1% is not recommended for composites. The coefficient of fragile crack resistance K_{IC} in comparison to the source material for graphene content 1% weight by weight slightly increases from 5.9 MPa $\text{m}^{1/2}$ to 6 MPa $\text{m}^{1/2}$. A slight improvement in crack resistance may be associated with the effect of propagating cracks with graphene flakes. In composites with a higher graphene content (2% and 3% by weight $K_{IC} = 5.4 \text{ MPa} \times \text{m}^{1/2}$), what results from it, that due to the increase in porosity and the thickness of the flakes, the carbon phase is not a major resistance to propagating cracking. The hardness decreases with the content of graphene in the composite. The highest graphene content is found in the composite with 1% weight graphene and 1477 HV, the lowest graphene content is found in the composite with 3% graphene weight and 1365 HV. A slight decrease in hardness in composites is typical for the addition of a component of lower hardness [95].

Moreover, the literature indicates that in the case of ceramic composites, in addition to improving the resistance to fragile cracking, the addition of graphene to ceramics improves the screening properties against electromagnetic radiation (up to 99% for graphene structures of about 30% mass) [96], electrical conductivity [97] and in some cases

hardness (even double the hardness after adding about 1.5% vol. graphene flakes) [98].

3.3 Metallic composite materials

Carbon in various forms, such as nanotubes, graphite and graphene, can be used as an additive to metallic sintered composites. The results contained in the paper by Chmielewski and co-workers [99] showed that graphene addition to copper composites obtained by powder metallurgy reduces the mechanisms of peeling. In addition, it increases the wear resistance and reduces the obtained values of friction coefficients of such composites in relation to unmodified copper sinter. The obtained composite materials were characterized by a high degree of density (above 97.5% of theoretical density). Microstructural studies have shown that regardless of the carbon form used (nanotubes, graphite, graphene), the porosity of the composite mainly occurs in the reinforcing phase area. In the case of carbon composites in the form of graphite or graphene powder, the formation of a continuous composite structure is observed, without visible microstructural defects. The addition of carbon, regardless of its form, has a positive effect on the reduction of the friction coefficient. The lowest coefficient of friction (0.35) was obtained for Cu-C composite with graphite nanopowder. For the other composites, including those containing graphene, the coefficient of friction in the steady state was basically identical and amounted to about 0.4. The main factor determining the value of the friction coefficient was the size and uniformity of coal distribution. The lowest coefficient of friction was obtained for the composite with the best carbon dispersion, that is, the composite with graphite nanopowder. The volume wear of the tested composites, which was compared to that of pure copper, was lower. The wear of the composite depended on the form of the contained carbon. Composites with graphite nanopowder and graphene have the highest wear resistance. The highest wear was obtained for composites with nanotubes.

Graphene was also used to protect the surface of copper and other metals against environmental conditions, such as temperature, humidity or corrosive chemicals, especially oxygen and carbon dioxide. Protection of metals against the effects of environmental conditions is based on the application of graphene or graphene oxide in the form of a suspension in water or an aqueous solution with hydrophobic properties on the metal surface [100].

In a separate study on the combination of graphene and metals, has been shown that graphene resulting from the combination of many crystalline grains is al-

most as strong as graphene in a homogeneous crystalline form. These studies dispelled doubts between theoretical simulations that predicted that grain boundaries would strengthen the material and earlier experiments that proved less strength of the connected grains than the crystalline graphene network. In addition, it was determined that the mechanical properties of graphene layer in graphene-metal composite effectively inhibited the growth of cracks caused by external forces and provided an increase in the strength of graphene-metal composite material.

Research works on the application of graphene for electrodeposition of nickel composite coatings were the first attempt to use and evaluate the advantages of this material in nickel composite coatings in order to increase their resistance to wear. In this work, the deposition of nickel graphene composite coatings was carried out with Watts bath with reduced nickel ion concentration, organic additives and graphene as dispersion particles. It has been experimentally proven that graphene flakes embedded in the nickel matrix increase the hardness and wear resistance of the nickel material. In the case of nickel material, the hardness was estimated at the level of 315, after graphene application this parameter increased to 452. In the case of wear tests, the analysis of the defects after the tests showed a reduction of about 50% after the application of graphene powder in the coating structure [101].

3.4 Graphene structure modified fibre composites

3.4.1 Linear textile products

The literature presents numerous studies on obtaining (spinning) graphene fibers [102, 103], the authors of which, while defining individual parameters of the obtained fibers, conclude that they may revolutionize the electronic, insulation or protective market in the future. Particularly noteworthy are the results of the study on graphene fibers obtained by the wet solution method [104]. These fibers were spun from a suspension of graphene oxide in a coagulation bath [105]. The fibers obtained are characterized by a porous structure and their surface roughness increases with the increase in the size of graphene “flakes”. It is worth noting that the tensile strength of the fibers reaches a value above 200 MPa, with modulus of elasticity of about 11 GPa. However, the authors of the publication [104] declare that the fibers obtained are characterized by very good thermal properties (defining, among others, their thermal conductivity).

Figure 7: Morphology of polypropylene fibres modified by reduced graphene oxide (PPF-RGO) (a) pristine PPF, (b) PPF-RGO -1 coating, (c) PPF-RGO – 3 coatings, and (d) PPF-RGO-5 coatings [113].

Using the wet solution method, sodium alligat fibers containing graphene were also obtained [106]. Analysis of the results showed that the addition of 4% graphene oxide is sufficient to increase the tensile strength of alginate fibers by 94%. The method of obtaining fibers from wet solution was also used to obtain chitosanic fibers doped with graphene oxide [107, 108] and fibers from regenerated cellulose with graphene [109]. For chitosanes doped with graphene oxide, a tensile strength of 165.8 MPa has been determined (unmodified chitosanes show a strength of 96.7 MPa). Such fibers may also have absorption properties, as demonstrated by testing their ability to absorb dyes, *i.e.* Congo red. On the other hand, the fibers from regener-

ated cellulose with graphene were subjected to the evaluation of mechanical and thermal properties. It has been proven that a small (0.2% by weight) addition of graphene improves the tensile strength by about 50% and strengthens the Young's module of fibers by 25%. In addition, the fibers showed excellent thermal and dynamic stability of heat transfer under high temperature conditions, which was confirmed by an increase in the initial decomposition temperature by 44°C.

Another method of obtaining fibers doped with graphene structures is the electrospinning technique. It was used to obtain carbon nanofibers with graphene content [110].

Electrospinning is a simple and effective technique for the production of polymeric fibers, in which electrostatic forces are used to produce fibers and nanofibers [111]. In order to obtain carbon nanofibers, the authors applied the technique of electrospinning of polyacrylonitrile fibers with different graphene oxide content and then their carbonization. The application of the electrospinning method also allowed to obtain nanofibers of polycaprolactone with graphene oxide and reduced graphene [113]. Similarly as in other cases, a significant increase in the strength properties of nanofibers was observed here, *i.e.* at 0.1% weight of graphene oxide, an improvement of these properties by 160% was achieved, while at 0.1% weight of reduced graphene oxide, an increase in strength by as much as 304% was observed.

Another important issue seems to be the addition of graphene to the fibers by surface application method. Ramasundaram and co-workers [113] used a three-stage immersion method to apply functionalized graphene oxide on polypropylene fibers (Figure 7).

In the first stage these fibers were washed several times in deionized water, then dried at 70°C and then immersed in xylene for 5 hours at room temperature. Then for 2 hours the fibers were placed in dimethoxy-amphetamine. The fibers swollen in this way were then placed in the dispersion of functionalized graphene oxide (the operating time was determined “overnight”). In order to remove the remaining solvent, the fibers were dried at 100°C in a vacuum for 5 hours. Polypropylene fibers prepared in such a way with a functionalized graphene oxide coating applied were reduced in an aqueous solution of hydrazine monohydrate (2g/l) at 100°C for 24 hours. After washing alternately with cold and warm water, the fibers are placed in a solution of surfactant (containing Tween 80) and subjected to ultrasonic treatment for 1 hour to remove unbound reduced graphene oxide. As a result, the fibers obtained were characterized by increased hydrophobicity, which recommends them for filtration applications.

In turn, Chen *et al.* [114] presented the method of applying surface graphene oxide on carbon fibers. In this method, carbon fibers, after being placed in acetone, were heated to boiling point for 12 hours, then transferred to the solution of petroleum ether and heated for another 12 hours. During this time a preparation of a uniform mixture of graphene oxide and graphene oxide functionalized by silane groups took place. The mixture was obtained by dispersion in deionized water and acetone of the above mentioned products and its treatment with ultrasound for 2 hours. After this stage, carbon fibers were placed in this homogeneous mixture containing graphene structures for 20 seconds to absorb graphene particles. The fibers were then

dried at 50°C in vacuum and after drying they were placed in a mold into which a resin based on 2-ethyl-methyl imidazole was injected. The mould was then introduced into the furnace for 8 hours (2h at 90°C, 2h at 120°C and 4h at 150°C) to obtain a hardened composite. The authors prove that using the method described above, the properties of the composite such as interphase shear strength (increase by 60%) are significantly improved.

Similar studies were carried out for aramid fibers [115]. The proposed method of graphene oxide application on the surface of these fibers allowed to increase their average tensile strength and mean interfacial shear strength by 7.9 and 44.33%, respectively, in comparison with unmodified fibers.

3.4.2 Flat textile products

The main current in the modification of flat textile products is the application of graphene on their surface using various methods, such as electrostatic coating or surface deposition, with a view to their further application in various types of applications.

Samad and co-workers presented the electrostatic method of coating the surface of polyamide fabric with reduced graphene oxide (Figure 8) using a two-stage process [116]. This process involves immersing a polyamide fabric in a solution of graphene oxide (2 mg/ml). The fabric is then dried at elevated (80°C) or room temperature to allow slow film formation. As a result, the fabric can be used *e.g.* as a piezo-resistive pressure sensor.

Spanish researchers proposed another method of obtaining flat textile products containing graphene oxide, including polyester fabrics [117]. This process involves placing polyester fabrics in a graphene oxide solution for 30 minutes, drying and further treating them with a sodium dithionate solution at about 90°C to reduce graphene oxide. The polyester fabrics obtained after applying several layers of reduced graphene oxide show conductive properties. Similar methods were also used for the coating of cotton fabrics [118, 119].

The obtained flat textile products modified with graphene structures were subjected to evaluation of the degree of protection against UV radiation and investigations enabling to determine the physical and mechanical parameters of fabrics, *i.e.* tensile strength or surface resistance. Increasing the UV resistance of cotton fabric was made possible by applying a nanocomposite based on chitosan and graphene to its surface. As expected, the effectiveness of UV protection was improved, and what is important, the

Figure 8: SEM images of rGO-coated Nylon[®] with uniformly coated rGO wrapping around individual fibers shown in the inset (a), a scissor-cut cross-sectional view of an individual rGO-coated Nylon[®] fiber showing rGO-coated surface and polymer core (b), pristine Nylon[®] fiber (c) and rGO-coated Nylon[®] fiber with a twist angle of 720° (d) and pristine Nylon[®] fiber (e) and rGO-coated Nylon[®] fiber with a twist angle of 1800° (f). Scale bars: Main figure 100 μm and Inset 10 μm (a) 10 μm (b–f) [116].

Figure 9: SEM micrographs of (a) lyocell and (b) GNs coated lyocell [123].

fabric obtained maintained its properties up to 10 water wash cycles [120].

Subsequent studies also confirmed increased UV protection of graphene modified cotton fabrics [121]. It was shown that even a small graphene content (0.4% by weight) causes a 10 times higher UPF value (from 32.71 to 356.74).

Research conducted in foreign centers in the field of strength and conductivity properties assessment also showed an increase in these parameters after introduction of graphene into the structure of the fabric. For example, for graphene silica fabric, tensile strength properties equal to 40 MPa were obtained. This fabric was also characterized by high thermal stability and absorption properties of microwave radiation [122].

In turn, lyocell fabrics modified with graphene oxide (Figure 9) were tested for surface resistance evaluation, whose value was found at $40 \Omega \times \text{sq}^{-1}$. This type of fabric was then used for the production of elastic electrodes [123].

4 Analysis of possibilities and determination of perspectives for graphene application in composite materials intended for the production of individual protection equipment

4.1 Technologies of polymer-graphene nanocomposites designed to monitor the state of ballistic composites structures

Sensors and advanced measuring systems have become very popular in recent years and the demand for this type of equipment is constantly increasing. The general principle of all sensors is to reproduce the physical/chemical/biological properties in the form of a recordable and interpretable diagnostic signal. They are commonly used for industrial production control, protection, communication, transport, measurement systems, research work, electronics, etc. Graphene, as a transparent semiconductor with zero energy gap, can be used in most of these devices. To this end, further fundamental research is required into the mechanical, optical and electrical processes taking place on its surface.

The general classification of sensors makes it possible to divide them into two groups depending on whether they require direct contact with the objects/sources of the recorded signal or not. The first group includes chemi-

cal, electrochemical, mechanical sensors, and the second group includes optical, optoelectronic, magnetic and electrical sensors. In both cases, solutions using graphene are possible. In particular, a great deal of research is carried out into bio-sensors on graphene substrates for diagnostic purposes, control of harmful substances and studies of the environmental status.

In the case of technologies used for monitoring composite structures, it can be stated that on the basis of worldwide research on carbon nanotubes and graphene, it is possible to build a strain sensor using graphene [124, 125]. It has now been proven from research into carbon nanotubes in composites that it is possible to construct a material that will also detect damage from carbon nanotubes. Deformations and failures are detected by determining the change in resistivity of the material under test. The essence is the admixture of the insulating material (*e.g.* polymers) with the conductive material which is graphene. For a critical amount of graphene flakes (expressed as a percentage of the volume or weight of a composite), the entire polymer-graphene composite begins to conduct an electric current (this percentage is called the threshold of electric percolation). The electrical conductivity in this case is mainly related to the quantum phenomenon of electron tunneling from conductors (graphene) through an insulator (polymer). The change of distance between graphene flakes, resulting from *e.g.* deformations of the composite, causes a change in the conductivity of the composite. Thus, the piezo resistive effect appears. also the graphene itself subjected to deformations shows the piezo resistivity effect related to the increased frequency of vibrations of carbon atoms [126]. However, in the case of graphene-polymer composite, tunneling has a greater influence on the piezo resistivity of the composite.

By measuring the changes in resistivity of a composite it is possible to determine its deformations. It is worth noting that for composites doped with graphene the piezo resistive effect is much stronger than for composites doped with carbon nanotubes [124]. Very high sensitivity is also achieved for the graphene-nanotube mixture. The smaller the dimensions of graphene flakes and the greater their share in relation to the share of carbon nanotubes, the greater the sensitivity of the material [127]. It also seems logical that the appearance of damage to such a composite, *i.e.* discontinuities, will introduce a change in the resistance of the composite that is not a result of deformations, which should be detectable. The application of polymer-graphene nanocomposite can lead to the formation of a deformation and damage sensor, which is ideal solution for monitoring the condition of structures. Moreover, this nanocomposite can be used as a matrix in traditional com-

posites used *e.g.* in ballistics or aviation, which leads to a situation in which the structure itself is a sensor and does not require the use of additional sensors (*self-sensing material*). It is worth noting that it is a sensor that measures deformations on its entire surface and not point-wise (such as Bragg's mesh), which is particularly important in the case of damage detection.

In addition, graphene sensors with a resistive layer changing the value of resistance under the influence of pressure or pressure were developed. Pressure sensors consist of a substrate layer, conductive layers, at least one resistive layer containing carbon material and polymer carrier, and a dielectric layer. The carbon material of the resistive layer is graphene flakes with the addition of carbon nanotubes, and the polymer carrier is alkyl polymethacrylate, methyl polymethacrylate or butyl polymethacrylate. The share of a polymer carrier in the resistive layer of such sensors is not greater than 98% by weight in relation to the mass of the layer. The developed pressure force sensors are characterized by the fact that with the increase of applied pressure the resistance decreases with linear characteristics in the system of logarithmic coordinate values. The change of resistance as a result of the operating pressure is due to the piezo resistive effect in materials based on semiconductor materials [128].

4.2 Graphene-enriched ceramic and polymer composites for innovative, ballistic and bulletproof armoring

Ceramic composite materials are used in ballistic applications, mainly as hard composite ballistic shields. In the case of such materials, two aspects are most important, namely the appropriate strength and weight. The emergence of new materials, *i.e.* graphene or manufacturing processes, makes it possible to reduce the weight of applications for ballistic applications and increase the ballistic resistance.

Over the last few years, work has been carried out on the use of graphene and its derivatives to produce composite materials improving ballistic resistance [129–131]. Domun *et al.* [130] presented experimental studies on the ballistic impact behavior of nano modified glass fiber-reinforced polymer (GFRP). The epoxy matrix of the GFRP was modified by the addition of graphene platelets (GNPs), carbon nanotubes (CNTs), combined hybrid hexagonal boron nitride nanosheets (BNNS/CNT), and combined boron nitride nanotubes (BNNTs/GNPs) nanoparticles (Figure 10).

Figure 10: SEM images of nanoparticles used in hybrid nanocomposites: (a) MWCNT; (b) f-GNP; (c) BNNS; (d) BNNTs [130].

Ballistic impact tests were carried out on GFRP laminates at two projectile velocities of 76 ± 1 m/s for full-field deformation measurements and 134.3 ± 1.7 m/s for perforation tests. The results of full-field deformation, exit velocity and energy absorption measurements from the ballistic tests show significant improvements in impact resistance for the panels made from nano modified epoxies relative to laminates with the unmodified epoxy matrix. The highest absolute absorbed energy was observed for the GFRP panels fabricated using the epoxy matrix loaded with BNNT/GNP at 255.7 J, 16.8% higher than the unmodified epoxy matrix. investigate the ballistic impact.

In turn Meng *et al.* [131] investigated behavior of multi-layer graphene plates up to 25 layers using coarse-grained molecular dynamics simulations. Through coarse-grained molecular dynamics simulations, authors showed that beyond a critical plate thickness, a cylindrical projectile penetrates the plate at a lower velocity than a spherical one. This counterintuitive phenomenon was explained by spalling-like failure for thicker plates, where the graphene layers at the bottom section undergo a wave-superposition

induced failure in the cylindrical case. Finite element simulations were carried out to show that in-plane tensile stress concentrates at the bottom section, resulting from the superposition of incident and reflected stress waves. A mechanics relationship was then proposed to describe the resisting pressure of the graphitic plate during ballistic impact. Meng *et al.* [131] indicates that the intensity of stress wave, which affects the spalling-like failure, depends on the projectile initial velocity, plate compressive modulus, and density. The findings presented in the paper reveal the existence of a new failure mechanism for multi-layer graphene systems, and provide theoretical guidance for future dynamic mechanical property characterization of graphitic barriers.

The investigations related to ballistic applications in various types of armoring were also carried out for hybrid, layered ballistic composites based on montmorillonite and epoxy glass fiber laminates. In these composites graphene in the form of nanoflakes added to the laminate fibers was used. The composites were subjected to ballistic tests for Class I and II A missiles according to NIJ Standard 0101.03.

On their basis it was found that the addition of graphene to the composite strengthened its resistance to missiles. In addition, it affected the destruction mechanism, through a significant increase in the delamination process. In the case of graphene-enriched composite, the effect of delamination of the outlet surface of the composite increased by about 557% with no changes in the inlet surface delamination [132, 133].

Shaojiu and co-workers [134] filed a patent application for the manufacture of three-layer ballistic shields in which the outer layers are aluminum alloys 5083 and 7A21 and the inner layer is made of silicon carbide reinforced with graphene. This layer is obtained by sintering at 700–750°C powder silicon carbide with a monodispersive mixture of graphene and ethanol. The proportion of silicon carbide by weight to the amount of graphene introduced is approximately 60:20%.

In turn, patent application No. CN 105272268 [135] presents a method of obtaining ultra-hard ceramic elements with ballistic properties made of the main ceramic phase, which is boron nitride and additives, *i.e.* diamond powder, graphene, carbon nanotubes or rare earth metals. The main ceramic phase (boron nitride) in the above mentioned ceramic elements accounts for approximately 70–92% by weight of the entire composite, which is obtained in two stages. In the first stage, the main ceramic phase is mixed with the additives and in the second stage, the sintering process of the obtained mixture is carried out. Sintering is carried out at temperatures from 1200°C to 1900°C and at a pressure of 30,000 – 60,000 atm. The composite material obtained is characterized by significant resistance to fragile cracking, bending strength, high rigidity and ballistic resistance.

Apart from the above mentioned data concerning the possibility of using ceramic structures with graphene addition in applications related to ballistic protection, several foreign patent applications can be indicated, covering the issues related to the use of polymer composites doped with graphene in this type of applications. Based on the patent US2015218730-A1 [136] it can be determined that it is possible to obtain a polymer composite containing graphene nanoparticles for the production of bullet-proof vests, ballistic protection or vehicle armor. In the invention described above, polymeric composites contain well dispersed graphene nanoparticles in the polymeric matrix. In addition, these composites can be obtained in both sheet and fiber form. In this process it is preferred to use polymers obtained by polymerization of the following groups: benzamidazobenzo phenanthroline, benzobisazole, pyrido-bis-imidazole. The polymerization is carried out in a solution with the addition of polyphos-

phoric acid at a suitable pH. The polymer concentration in the environment is selected so as to support the formation of anisotropic mixture. The polymer concentration value shall be between 5 wt% and 20 wt%. In contrast, for graphene nanoparticles from 0.1 wt.% to 70 wt.% for film or mold production and from 1 wt.% to 50 wt.% for fibers, but the size of the share is also related to the weight of polymer obtained in the polymerization process. Such composite shows high modulus of elasticity, strength, good electrical properties, thermal stability and electromagnetic shielding properties.

In addition, polymeric hybrid composites for personal protective equipment applications, including those that could be used in the construction of bullet-proof and fragment-resistant vests, were obtained by Kim and his co-workers [137]. They obtained a flexible polymeric blend of graphene and carbon nanotubes with increased strength. The obtained hybrid polymer in the form of a composite fiber containing graphene and carbon nanotubes is based on reduced graphene with grain size in the range of 100 to 1000 nm and functionalized by carboxyl groups. Graphene added to the composite is obtained by chemical exfoliation. Single wall carbon nanotubes are bound to a surfactant containing a hydrophilic sulphonate group, *i.e.* sodium dodecylbenzene sulphonate (SDB), sodium dodecyl sulphonate (SDS), Triton X-100, cetyltrimethylammonium bromide (CTAB). The following are used as polymers: polyvinyl alcohol or poly(methyl methacrylate). The polymer content can be adjusted from 20 to 80 wt.% depending on the molecular weight and coagulation time of the polymer.

The research shows that graphene coatings are characterized by a much higher impact resistance of a projectile compared to metal coatings. The force of resistance of graphene flakes, consisting of one to twenty layers, is greater than 0.5 to 6.5 times in comparison to 5 atomic layers of steel, gold or aluminum coatings [138].

4.3 Application of textile composites modified with graphene structures in individual protection measures

Chapter 4 presents the results of research on the manufacture and properties of linear and flat textile products, which indicate their applicability also in aspects related to personal protective equipment. Therefore, a literature research was carried out on the use of fibrous materials, *i.e.* aramids or polyethylene in PPE applications (*personal protective equipment*), including ballistic ones. As Husain's work [115] showed, there is a possibility of obtaining

aramid fibers strengthening with graphene. These fibers are obtained by the use of plasma copolymerization by means of which aramid functionalization is carried out, and then single-layer graphene sheets are attached to the fibers. This modification was carried out in several stages.

In the first stage, the fiber structure was functionalized by attaching amino groups, which was carried out by immersing the fibers in alkaline ammonia suspension with pH=9. Next, graphene sheets were functionalized by introduction of hydroxyl and carboxyl groups in the process of oxidation in an aqueous suspension of pH=6. As a result of chemical interactions between particular functional groups, amine chemical bonds are formed which enable a permanent connection of aramid and graphene structure. Moreover, the authors determined that the mean value of tensile strength for modified fibers showed an improvement of over 79%, while the shear strength at the phase boundary in the modified composite model increased by 44.7%. A similar modification was made in the case of Kevlar oligomers [139]. Kevlar fibers can also be covered with a layer of conductive material doped with graphene, using the layer-by-layer method. The fibers are covered with polyurethane which is used to bind Kevlar and Graphene. Strongly adhering single-walled graphene porthole obtained a permanent conductivity of 65S/cm, without causing significant mechanical degradation of Kevlar fibers [140].

Graphene modified fibers can be used in applications such as: ballistic helmets [141]. In applications of this type, graphene combined with thermoplastic resin is used as an impregnation of fibrous material to improve ballistic resistance at the same time. Moreover, the patent investigation showed the presence of applications for the use of graphene in the construction of bulletproof and fragment-proof vests [142]. In this type of applications graphene was introduced into the structure of Kevlar fibers, which improved their parameters, *i.e.* resistance to deformation, elasticity or mass of the product.

As the research has shown, graphene-based materials achieve higher puncture resistance, which is associated with very high graphene break stress values ranging from 0.25 to 0.30 and significantly higher than the values obtained for polymeric materials (0.04) currently used in the construction of ballistic armor. Due to this fact, graphene may become one of the most effective additives for composite products in lightweight ballistic clothing [143, 144].

Recent research has centered on investigations of ballistic performance of Kevlar fabric impregnated with different shear thickening fluids (STFs). Ballistic experiments were performed on fabric treated by different STFs, and different failure modes including yarn slipping, extraction,

and breakage in shear failure were obtained. The results showed that STF reinforced with graphene is better at preventing the yarns from slipping, and the single yarn pull-out force is almost 5 times more than pure STF. Moreover, reinforced STF also has a significant influence on the ballistic limit and energy absorption of Kevlar fabrics. And the increased amplitude of energy absorption is almost 20% more than the pure STF/Kevlar load case [145].

Naveen *et al.* [146] investigated the effect of adding GNP (graphene nanoplatelets) to improve the mechanical and moisture resistant properties of Kevlar/cocos nucifera sheath /epoxy hybrid composites. The results revealed that the addition of GNP improved the tensile, flexural, and affect properties of laminated composites. This is mainly due to a better dispersion of the rigid GNP which enhances the mechanical interlocking capability by bridging individual plies through a strong interface. However, the optimal wt.% of GNP varies with different laminates. An FTIR analysis reveals that the functional groups present in the GNP can form strong interactions with Kevlar, cocos nucifera sheath, and epoxy resin. From the XRD analysis, authors were found that the addition of GNP improved the crystallinity of the hybrid composites. From the overall analysis, it has been concluded that these GNP-modified epoxy hybrid composites can be effectively used in load-bearing structures in the automotive, aircraft, and defense sectors where a higher strength to weight ratio is a prime requirement.

In addition, investigation of Kevlar-epoxy laminated composites modification by graphene was performed by Rahman *et al.* [147]. Graphene and nanoclay with different weight fractions were added into the epoxy matrix of Kevlar-epoxy (KE) composite panels (Figure 11), and the effects of these nanomaterial inclusions were evaluated for low-velocity impact, damage analysis, and UV degradation. The low-velocity impact study showed that the absorbed energy of the KE composite panels (both baseline and nanoclay-reinforced) demonstrated well the established elastic strain energy theory. As the volume fraction of nanoclay increased, the impact resistance also increased. The test panel with the 10 wt% nanoclay-filled epoxy composite responded with the highest impact load (26% more than baseline) and recuperated the most of the energy (24% more than baseline). However, the graphene inclusion did not contribute to an increase in impact resistance. On the other hand, both nanoclay and graphene inclusions reduced the damage area and increased the resistance to UV degradation and water absorption.

Figure 11: SEM images of : (a) 2 wt% NC-reinforced, (b) 5 wt% NC-reinforced, and (c) 5 wt% G-reinforced epoxy matrices (NC and G are marked with circles) [147].

5 Challenges and new trends in graphene composites

Research on graphene technologies has been conducted for around 40 years. This subject is still important and attracts great interest both in the scientific community and industry. A brief overview of the publications and patent licenses for graphene shows a growing interest in this field since the discovery of graphene: data obtained from the Web of Science database indicates a steep increase in the

number of citations, which is an indication of the scientific impact of graphene research. The expanding number of research papers, patent licenses and research programs (e.g. Europe Graphene Flagship) in recent years shows the development of innovation in this subject. Market reports [148, 149] estimate that the first applications that are now being commercialized include composite functional coatings, graphene batteries, low-cost printable electronics (based on graphene inks), photodetectors and biosensors. More advanced applications such as solar cells and flexible perovskite panels, supercapacitors, water treatment,

Figure 12: Graphene application roadmap.

neural interfaces, and flexible devices will be available from 2022. It is also estimated that graphene-related materials will be adopted in drug delivery, spintronic devices, wireless network and fuel cells from 2030 (Figure 12).

However, there are also several challenges in the manufacturing of graphene composites, such as industrial-scale production that is not yet fully developed, differences in the quality of the obtained graphene and graphene-based products, comparatively high production costs, a lack of standards, no precise data on environmental impact, and safety issues.

The problem of production scaling is multi-faceted, including in terms of technologies related to the use of graphene-based products. Currently, most graphene research is conducted on a laboratory scale, which determines the widest ranges of variability of the basic parameters of individual processes. However, some of these parameters are subsequently omitted or postponed for the period of research conducted on a semi-technical or industrial scale. These factors often become problems of the first order when increasing the scale of production. The main problems associated with increasing the scale of production are as follows:

- The stability, controllability of manufacturing, and optimization of individual technological processes is difficult to achieve.

- Production cost and time. Cost is an important factor in itself, and has reduced considerably since the first commercial appearance of graphene. Over 2 years the price of sheet graphene has dropped to one-third of its starting price, while the price of powdered (including liquid) graphene has dropped to one-quarter. However, the initial material cost is still high, promoting applications that exploit multiple graphene properties, and leading to initial adoption of high-margin applications.
- Maintaining quality is difficult in large quantities of graphene materials.

The quality of graphene composites and the sustainability of supply chains are considered highly important. Sustainability is essential to ensure the scalability of the production process and affordability of the material, yet is uncertain due to an immature market and technical issues on the production scale. Conversely, the quality of composites will determine its performance in the end applications, as the quality of graphene has a significant impact on properties that are specific to graphene and composite products made on its basis. In this case, the quality very much depends on the fabrication process of the material, and this is still undergoing extensive research in numerous projects [150]. The quality of composites used for the production of PPE is determined by factors such as structural defects and impurities on the graphene, degree of dispersion, the num-

ber of different layers, degree of functionalization, and the compatibility with the composite materials and ratio aspects [55].

Improving the dispersion and interfacial interactions between the graphene and composite matrices are key challenges to obtain property improvements in their composites. There have been some reports that reduced graphene oxide contains some oxygen-containing groups, which will facilitate its dispersion and interaction with polymer matrices [151]. In fact, in many cases reduced graphene oxide has a pronounced tendency to restack during the thermal and chemical reducing processes and is difficult to uniformly disperse in some polymer matrices due to the removal of most functional groups. Functionalization should also be an important route to prevent restacking and improve the interfacial interaction.

An important issue for the further development of graphene-based technology is understanding the interaction between graphene and biological systems. Tests to determine the impact of graphene and its derivatives on the environment are necessary before introducing solutions to commercial products. However, the assessment of the ecological risk is multi-faceted and requires the development of many test methods and the selection of exposure indicators. Graphene is a new nanomaterial, so the mechanism of its harmfulness remains, in many aspects, a mystery. Due to the growing interest in nanotechnology, there should be more attention focused on the potential impact of graphene and its derivatives on the environment. Little is known about the effects of long-term exposure to graphene products and epidemiological data are not yet fully available. The most important global problem appears to be the penetration of nanoparticles into the ecosystem and their accumulation in trophic chains [152]. A review of the literature shows that toxicologists are attempting to assess the degree of graphene oxide toxicity in both *in vitro* and *in vivo* tests. Several types of bacteria, mammalian cells and animal models are used for this purpose [153]. The test results collected so far indicate that the toxicity of graphene oxide is determined by several factors, such as flake size, the presence of functional groups, and chemical purity [154, 155]. It is suspected that the first toxic effect of the implementation of graphene oxide into the environment can be observed in populations of microorganisms living in water or soil (bacteria, algae) that are found in the bottom of the food chain.

Another challenge in the development of graphene-based technologies and products is the lack of well-defined standards. Industry has identified the lack of standardized materials and characterization methods as one important factor slowing innovation in the field of

graphene. The issue can be illustrated by two questions: “What properties of graphene or a related material do I need to know and control in order to reliably achieve the desired function in my application?” and “Who can guarantee that their raw material meets my specifications in every single production batch?” The first question is often surprisingly hard to answer, for example in the case of polymer composites using graphene as a filler, where flake size, surface functionalization, lattice defects, aggregation behavior, material processing, and many other factors have a decisive impact on the performance of the composite. Finding the right supplier in such a case may be an additional challenge. Standardization lays the basis for solving such issues. It will help enable better quality control, improve reliability and trust, and lower one of the key barriers to graphene innovation and commercialization. Work on standards in the field of graphene and related materials should be focused on: characterization methods, sample preparation, data analysis and terminology [148].

Despite all the challenges and problems arising from the implementation of technology based on graphene and its derivatives, further progress is estimated in both science and industry. These materials are at the introductory stage of the product lifecycle and significant development is expected in terms of its applications in the next 5 to 6 years.

6 Conclusion

Due to the constant increase in the importance of research on graphene and its structures, the article reviewed the literature with the aim of analyzing the properties of composite materials containing graphene and determining the perspectives of their application in the manufacturing of PPE - Personal Protective Equipment.

The literature review carried out has shown that graphene and its derivatives can be successfully used as additives to ceramic, metallic, fibrous and elastomeric materials. The use of graphene in this type of materials allows to improve a number of physical and mechanical properties, such as resistance to brittle fracture, tear and tensile strength, conductivity or Young's modulus, thanks to that the composites doped with graphene can be used in many applications, including various chemical, electrochemical, mechanical and optical sensors, as well as in creating new personal protection against firearms.

However, the basic application requirement determining the further development of graphene technologies is to create reliable, cheap and easy to scale manufacturing

techniques. The relationship between ease and cost of production and the quality of the material is particularly important. In addition, an important aspect of the possible use of graphene in personal protective equipment, which was not, however, addressed in this review, is the safety of use and the impact of graphene structures on living organisms. Therefore, it is advisable to carry out numerous studies aimed at estimating the influence of graphene on living organisms.

In the framework of this work, the literature data were reviewed in order to verify the applicability of graphene and its derivatives, such as graphene oxide in the manufacture of personal protective equipment and to determine the effect of graphene on the physical and mechanical properties of composites and the protective properties of the products and equipment intended to protect the health and life of users.

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