advances
in Technology

Review

Review on Carbon Black and Graphite Derivatives-based Natural Rubber Composites

W. D. M. Sampath,[a,b,*] C. A. N. Fernando,[a] and D. G. Edirisinghe[b]

[a] Department of Nano Science Technology, Faculty of Technology, Wayamba University of Sri Lanka, Kuliyapitiya 60200, Sri Lanka
[b] Rubber Technology and Development Department, Rubber Research Institute of Sri Lanka, Telawala Road, Ratmalana 10390, Sri Lanka

Email correspondence: wikcramage@yahoo.com (W. D. M Sampath)

Abstract

Functional materials based on the crystalline allotropes of carbon have garnered tremendous interest from researchers in chemistry, physics, and material science for a long time. This paper reviews studies carried out on carbon black and graphite derivatives, their properties, and manufacturing applications. Graphite derivatives such as graphene, graphene oxide, reduced graphene oxide, expanded graphite, and graphene quantum dots are reviewed, along with a discussion of their synthesis and advantages. Generally, carbon black and graphite derivatives are incorporated into the polymeric material to enhance the performance of the end material. Recently, much attention has turned to the structural and electronic properties of carbon-based polymeric materials. Hence, at present, graphite-based polymeric material is the hottest topic in physics and materials science due to excellent electric and thermal conductivity, optical, mechanical properties, etc. The most common and widely used filler for rubber in the industry is carbon black due to its excellent physico-mechanical properties, thermal stability, oil resistance, etc. Therefore, carbon black and graphite derivatives incorporated composites of natural rubber have been reviewed in detail, along with a discussion of the current limitations and challenges of these exciting materials.

Keywords: Carbon black, graphite, graphene oxide, reduced graphene oxide, natural rubber

Introduction

Natural rubber (NR) is chemically defined as cis-1,4-polyisoprene and it is obtained from the *Hevea Brasiliensis* tree as the milky colour liquid which is called latex. In addition, latex contains small amount of non-rubber materials such as proteins, carbohydrates, lipids, metal ions and inorganic ions. Generally, latex is isolated by acidic solutions, and washed with water then processed into sheets. Developments in natural rubber elasticity, strength, thermal stability, and hardness are obtained by vulcanization usually in the presence of vulcanizing ingredients namely, sulfur, accelerator, and activator and other compounding ingredients such as fillers, resulting in a three-dimensional network [1]. Further, presence of crystallites acting as further cross-links in the network structure and their alignment in the direction of stretch, explain the outstanding physico-mechanical properties of NR [2].

In industrial applications, NR is compounded with different types of fillers to improve the physico-mechanical properties such as modulus, stiffness, stress softening effect, wearing and tearing resistance, hardness, tensile strength, etc. as well as electrical and thermal conductivities, optical properties, dynamic properties, barrier properties, etc. [3,4]. Further, rubber-filler interaction is one of the important factors that determine end properties of rubber composites. Therefore, carbon-based fillers are widely used as reinforcing filler with NR and synthetic rubber and the importance of carbon black (CB) fillers in the rubber industry been well known for many years. Essential features of CB filled polymer composites are influenced by particle size, surface area, and surface chemistry of carbon black. Furthermore, CB acts as a physical crosslinking agent especially at high filler concentrations due to polymer-filler and filler-filler interactions which lead to the formation of a continuous filler network held by weak van der Waals forces. In addition, carbon-based fillers which are based on graphite derivatives are widely used for different polymer-based industrial applications namely sensors, solar cells, fuel cells, electromagnetic interference

shielding, etc. [5]. Further, CBs are mostly used as reinforcing fillers in tire productions and automobile items [6]. Furthermore, carbon-based fillers are utilized for special industrial applications such as black colour pigments in plastics, paints, inks, and conductive polymers [7] and they are also used as ultraviolet (UV) stabilizers in polymers to prevent their degradation under the influence of UV light [8]. Nowadays, carbon-based fibers and graphite derivatives are the most commonly used conductive components to incorporate conductivity to polymer networks due to carbon fiber forming a strong linkage with polymer materials [9]. Carbon-based fillers are categorized in different forms namely, carbon black, carbon fiber, carbon nanotube (CNT), graphite derivatives, etc. Therefore, most of the properties of carbon-based filler incorporated polymer composites have been significantly changed due to characteristics of filler particles [3].

This paper presents a brief impression of studies carried out on natural rubber composites based on carbon-based fillers consisting of different properties such as electrical and thermal conductivity, optical and physico-mechanical properties. Further, developments utilizing graphite-based derivatives for special industrial applications are also reviewed in this paper.

Types of Carbon-based Filler

The different types of carbon-based fillers are CB, carbon fiber (CF), graphite (G), graphene oxide (GO), reduced graphene oxide (rGO), expanded graphite (EG), graphene quantum dots (GQDs), single and multi-walled carbon nanotubes (SWCNTs and MWCNTs), etc. Physical and chemical characteristics of these fillers vary according to their surface morphology, chemical structure, surface area, solubility parameters, etc. [10]. At present, carbon fillers play a vital role in our day to day life via innovative applications and origination of new kind of valuable materials. Therefore, some important details of carbon-based materials are described below.

Carbon Black (CB)

CB is composed of fine particles and it mainly consists of carbon. Various features of CB are controlled in production. Further, CB is a group of materials including furnace, thermal, and acetylene black [11]. CB shows a very complicated structure when observed through electron microscopy and the particles appear in spherical shape. The spherical shape CB particles of different sizes, connected as a chain is called a "structure". Carboxyl and hydroxyl groups have been found on the CB surface [11]. CBs are graded according to surface area and measurements of the size of structure [12]. Moulin *et al.,* reported that the greatest surface area is established on the furnace and thermal blacks.

Moreover, CB particle size and its distribution are most important for physical properties and end applications. Other than that, the smaller the particle size, the greater the blackness of CB, but dispersion becomes very difficult due to an increase in the coagulation force. According to Figure 1, particle size and geological structure of CB are directly affected by dispensability and darkness of CB particle. Therefore, CB with a larger structure represents superior thermal and electrical conductivity [11].
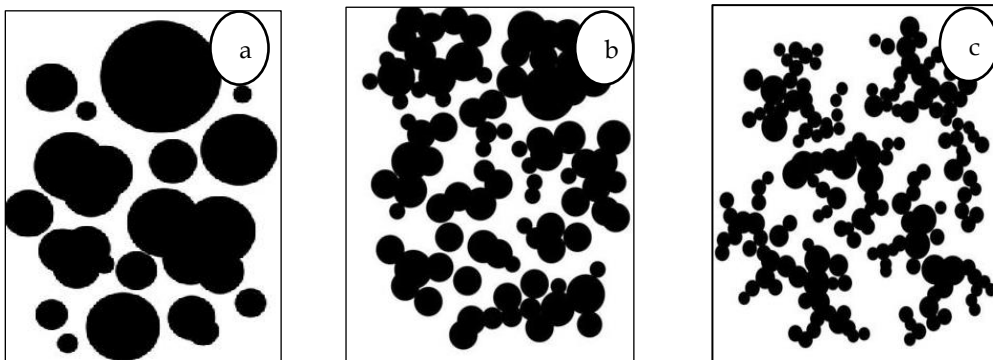
Figure 1. Carbon Black Structure (a) Low Structure (b) Moderate Structure (c) High Structure (Jebur, 2018).

Another important factor is the surface area, which is represented as an indirect correlation with CB particle size. There are two methods that have been used to determine the surface area of CB namely, iodine

absorption and nitrogen absorption methods. According to the surface area, thermal black is categorized as an N900 series, while furnace blacks fall within the N100 to N700 series. "N" indicates normal curing material. Therefore, the largest particle size of CB indicates thermal black and it has the lowest surface area. In contrast, furnace black has the smallest particle size and hence it has the highest surface area. In addition, surface area of CB depends on porosity and also, porosity influences certain industrial applications and properties at higher CB loadings [11]. CB is used as a reinforcing filler for most polymer materials, especially natural and synthetic rubbers, owing to the uniform dispersion of CB in the polymer matrix [13].

Further, failure properties of rubber composites such as modulus, elongation at break and tensile strength are significantly improved with CB reinforcement. Degree of reinforcement by CB varies with number of factors such as particle size, geological characteristics of particles, and interface characteristics [14].

Carbon Fiber (CF)

CFs have been made of at least 92 wt% (mass fraction) carbon, usually in the non-graphitic state. CFs are used for the reinforcement of various polymers since they have excellent strength to weight ratio, good thermochemical stability, and high creep resistance [15]. In addition, CFs are particularly attractive for power generation, automotive, and aerospace applications owing to their low density [15]. Carbon filaments have been used as the world-first application in light bulbs the late nineteenth century. CFs have been made using different techniques namely polyacrylonitrile (PAN), pitch, rayon, and polyethylene [16]. PAN technology was found to be the best in relation to performance and has been used in the production of a wide range of products, from ultra-filtration membranes to high-quality carbon fibers [16]. Further, properties of CFs strongly depend on the manufacturing process and starting precursor material [17]. Moreover, production of high property CFs from the precursors has been categorized as thermal stabilization,

carbonization, polymerization of the precursors, graphitization, spinning of fibers, etc.

The mechanical performance of CFs, such as Young's modulus and tensile properties, are mostly controlled by the choice of the precursor molecule and fiber processing conditions, which, in turn, defines the features of CF structure, such as crystallinity, molecular orientation, carbon content, density, etc. [16]. Further, according to CF structure and degree of crystallite orientation, together with the mechanical properties, CFs have been categorized into various forms namely ultrahigh-modulus (UHM), high-modulus (HM), intermediate-modulus (IM), high elastic modulus (HT), and low elastic modulus (LM) [18].

Furthermore, CFs could also be categorized according to its commercial availability. Therefore, they have been classified into three forms such as high performance (HP), general-purpose (GP), and activated carbon fibers (ACF) [19]. GP-CFs are used in low-performance applications due to low tensile strength as well as low modulus. HP-CFs are characterized by their superior mechanical strength and modulus and mostly used in carbon fiber reinforced polymer composites (CFRPs) for the aircraft industry [19].

Graphite

Graphite is a soft, shiny black colour mineral. It is a very useful industrial mineral, which has many chemical and physical properties that are facilitated in many morphological situations. Table 1. shows some important physical properties of graphite material [20]. These properties are gained from structural characteristics. Carbon atoms are covalently bonded to three other carbon atoms and one electron is not bonded. C-C chemical bond length of the material is short and gives rise to high strength.

Amongst other filler materials, graphite more especially expanded graphite merits special interest because of its abundant availability at a relatively low cost, lightweight and easy functionalization when compared to other carbon allotropes [21]. Graphite is a layered filler

material, consisting of a special structure where carbon molecules are attached by covalent bonds to other carbons in the same plane with a weak van der Waals force between the successive layers [22]. Carbon atoms of graphite are strongly bonded to only three other carbon atoms, two-dimensional layers, that are very stable, but where each graphite layer is only weakly connected to adjacent graphite layers by weak van der Waals forces. As a result, hexagonal layered structure is arranged. The presence of an unpaired electron makes graphite an excellent electrical conductor within the plane of the layers. Therefore, graphite is used as a good conductor of electricity similar to electrodes. Also, graphite exhibits good thermal and electrical properties as shown in Table 2. [20,23].

Table 1. Physical properties of graphite

Property	Value
Crystalline form	Hexagonal
Density at 300 K, 10^5Pa	2.26 g/cm^3
Atomic volume	5.315 cm^3/mol
Sublimation point at 10^5Pa	4000 K
Triple point	4200 K
Boiling point	4560 K
Heat of fusion	46.84 kJ/mol
Heat of vaporization to monoatomic gas	716.9 kJ/mol
Pauling electronegativity	2.5

Moreover, graphite has a high melting point of ~3,550 °C, but in the presence of oxygen will begin to oxidize at temperatures >300 °C and can be induced to sustain burning above 650 °C, given suitable conditions; the rate of thermal oxidation is slow, but increases with increasing temperature [24].

Table 2. Thermal and electrical properties of graphite

Property	Value
Heat of combustion $\triangle H_{co}$ @ 25°C and constant pressure to form CO_2 gas	393.13 kJ/mol
Standard entropy $\triangle H$ at 25°C	5.697 - 5.743 J/mol.K
Entropy $\triangle S_{298}$	152.3 J/mol.K
Enthalpy $\triangle H_{298}$	716.88, kJ/mol
Specific heat @ 25°C	0.690 - 0.719 kJ/kg.K
Thermal conductivity @ 25°C	398 W/m-K
Coefficient of Thermal Expansion	1.2-8.2x10^{-6} °C
Electrical resistivity	5x10^{-6}-30x10^{-6} Ω.m

In addition, there are three types of natural graphite and these depend on the type of ore deposit. They are namely lump graphite, flake graphite, and amorphous graphite [25]. Lump graphite is considered the most valuable, widely applicable, and the highest quality form of natural graphite. Further, lump graphite has better electrical and thermal conductivity, and also it has the highest degree of cohesive integrity compared to other types of natural graphite. Lump graphite is easy to mold and can be formed into solid shapes without any binder addition. Therefore, lump graphite is highly used for industrial applications such as lubricants, batteries, electrodes, etc. Another important natural graphite is flake graphite which is generated in either metamorphic or igneous geologic environments and it consists of graphite ranging from 80 to 90 % [26]. Flake graphite has better electrical properties compared to amorphous graphite since amorphous graphite has a graphite content ranging from 25 to 85% [26]. Hence, amorphous graphite indicates the lowest graphite content compared to the other two natural graphites. On the other hand, graphite is broadly used as an engineering material as it has good mechanical strength and compressive strength, which varies

from 20-200 MPa [23]. Therefore, graphite is utilized for variety of applications such as piston rings, thrust bearings, journal bearings and vanes.

Further, according to the previous study, graphite has been used for preparing polymer composites for different industrial applications and graphite/polymer composites are prepared in three different techniques such as in situ polymerization, melt intercalation, and solution casting techniques [27]. Furthermore, the morphological image of preparation of graphite filled polymer composites could be indicated according to Figure 2. Further, according to the manufacturing requirements and to enhance required properties, graphite had been derived in different forms such as graphene oxide, reduced graphene oxide (rGO), expanded graphite (EG), graphene quantum dots (GQDs), etc. These are called graphite derivatives.
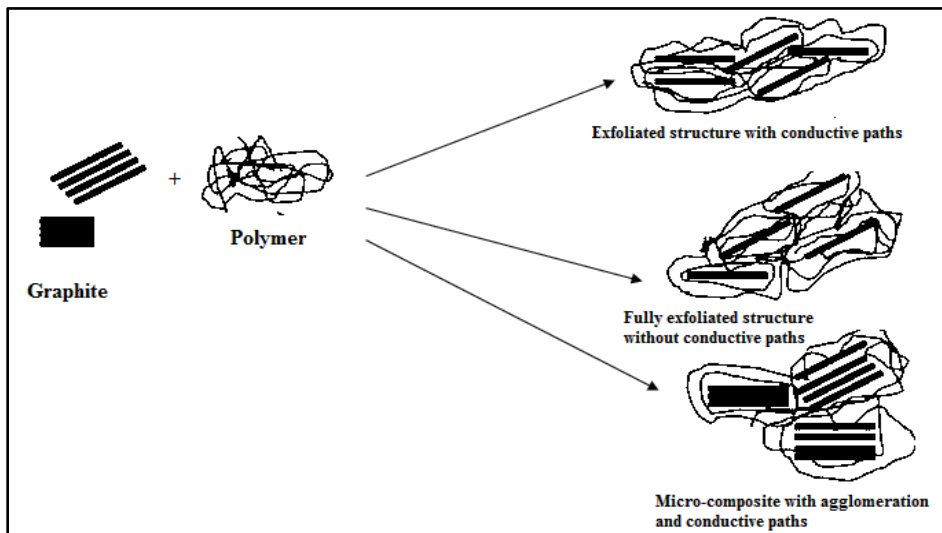

Figure 2. Morphological image of graphite filled polymer composites [26].

Graphene Oxide (GO)

GO is a single-atomic-layered material formed by the oxidation of graphite that is very cheap and readily available and conventionally it is called graphite oxide. As reported in literature, GO has been synthesized using different chemical methods such as Hummer's method, modified Hummer method, Staudenmaier method, etc. [28, 9, 29, 30]. Recently,

Kumar *et al*. have reported a new method to synthesize GO. They have synthesized GO sheets via electrochemical method coupled with oxidation process [31]. One of the interesting methods for synthesis of GO was using improved Hummer's method [32].

Figure 3 illustrates the formation mechanism of GO via Hummer's method [28]. Further, GO is used in different industrial applications due to the presence of oxygen containing functional groups such as -OH, -C-O-H, -COOH, -C=O attached to graphene layers as shown in Figure 3. Therefore, GO exhibits good hydrophilicity and hence its dispersibility in water is excellent [33]. At present, GO has attracted remarkable attention owing to its unusual structural, physicochemical, electrical and thermal conductivity, optical and mechanical properties [9]. Additionally, GO is highly considered as a reinforcing agent in the development of different polymer composite systems because of its superior electrical and thermal properties [34].
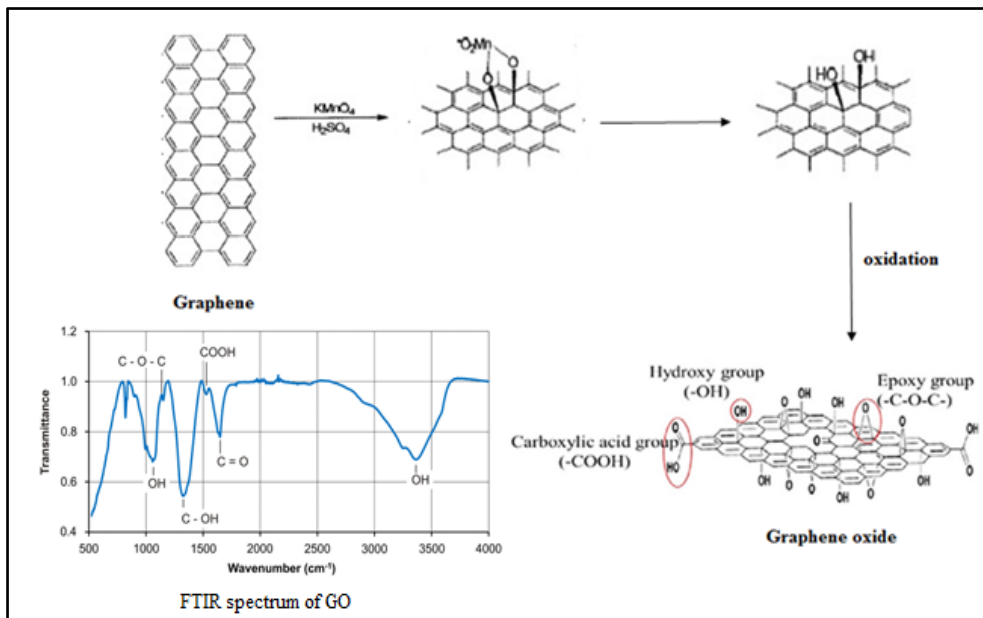

Figure 3. Formation mechanism of graphene oxide [28].

GO is not defined as a fixed material as it could be modified into different forms according to the required properties. GO has been modified to different varieties, namely expanded graphite, redusable

graphite, graphene quantum dots, graphene nanosheet, etc. [28]. In addition, GO might be used as a coupling material between polymer and filler as GO surface has good chemical functionality. Further, different functional groups could be grafted onto the GO surface according to research requirements.

Expanded Graphite (EG)

EG is modified graphite, which has a layered structure with interlayer space. Typically, the particle size of EG ranges from 10 to 30 μm [32]. EG is produced by abrupt expansion and exfoliation of expandable graphite in a furnace around 800–1000 ℃ [35]. When considering the structure of EG, it is similar to natural flake graphite. Unlike GO, EG has a large interlayer space [36] and it could be confirmed using scanning electron microscopy (SEM) images of it [35] and, according to Figure 4(a). EG is a loose and porous vermicular material and it basically consists of parallel boards, which collapse and deform desultorily, resulting in many pores of different sizes ranging from 10 to 50 μm (see Figure 4(b)).
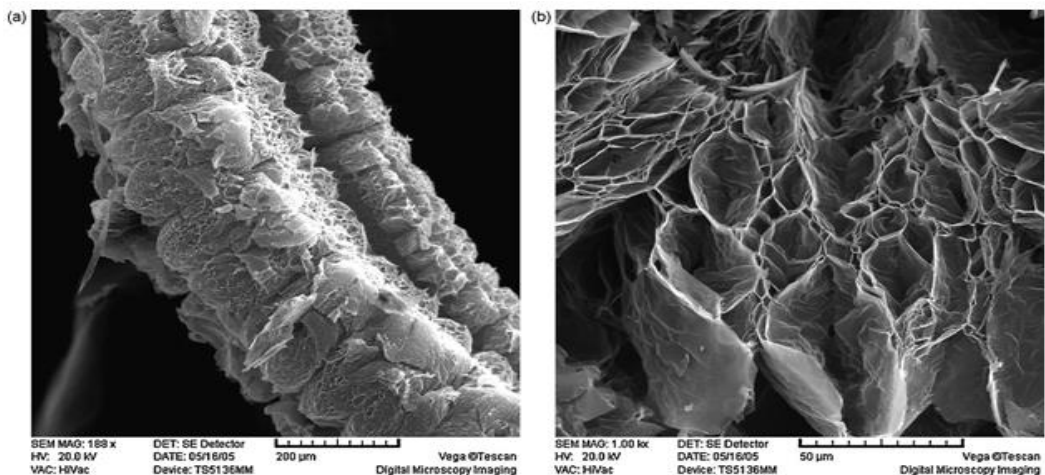
Figure 4. SEM images of expanded graphite at different magnifications (a) 200 μm (b) 50 μm [35].

In addition, EG is used to increase the compatibility of organic phase change materials due to its low density, high porosity, high thermal conductivity and low cost [37]. In a previous study, EG had been used

to increase the compressive strength of pure cement material and Yang *et al.* found a remarkable improvement of compressive strength when 10% of EG was added to the pure cement paste. Further, EG has been developed as a thermal energy storage material for building construction applications [38].

Reduced Graphene Oxide (rGO)

GO obtained from graphene includes oxygen in the functional groups. By reducing GO, these oxidized functional groups are removed to obtain a graphene material as shown in Figure 5. This type of graphene material is called reduced graphene oxide (rGO). However, different methods have been used to synthesis rGO via thermal, chemical, physical methods, etc. [39]. In addition, rGo had been synthesized from commercial expanded graphite [32]. rGO is widely prepared by chemical reduction technique, but this technique is highly disadvantageous because reducing agents are mostly harmful to the environment and highly toxic [40].

Reduction of GO by thermal treatment relies on the decomposition of oxygen groups into CO and CO_2 gases at elevated temperatures [41]. Therefore, the thermal exfoliation technique is considered as the most viable method since this method is fast and eco-friendly as it does not require the use of any solvent or reducing agent [42]. Further, Fe powder, hydroquinone, hydroiodic acid, sodium, sodium borohydride, hexamethylenetetramine are frequently used for synthesis of rGO [41]. In addition, rGO exhibits good thermal and electrical properties and hence would help to make good electronic devices such as supercapacitors, transistors, batteries, etc. [43]. Some other properties of rGO are shown in Table 3 [43, 44]. Tarekegne *et al.* [45] reported that, when graphene oxide is reduced to graphene, the oxygen-containing functional groups disappear. Tarekegne *et al*. [45] found that the suitable method to synthesis rGO is the Tour method as it is a less hazardous and more efficient method for graphite oxidation because of cost-effectiveness, non-toxicity, easy to handle and

environmental friendliness.

Table 3. Properties of rGO

| Property	Value
Density (g/cm^3)	1.91
Electrical conductivity (scm^{-1})	4.2×10^{-5}
Humidity (%)	3.7-4.2
Resistivity (Ωm)	23.7×10^{-3}
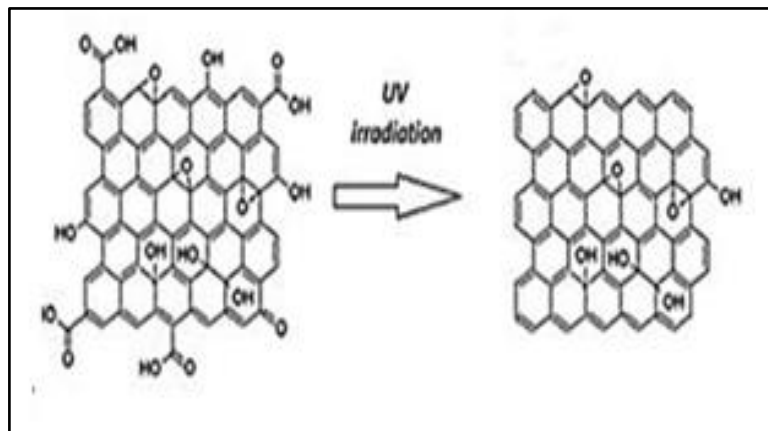
Figure 5: Transformation mechanism of GO into rGO.

Graphene Quantum Dots (GQDs)

GQDs are defined as graphene nanosheets that are less than 100 nm [46]. At present, GQDs have been focused for nanoscience and nanotechnology due to superior properties, such as stable fluorescence, excellent solubility, low cytotoxicity, high surface area, etc [47]. Number of top-down and bottom-up methods have been used to synthesize GQDs (see Figure 6) including hydrothermal, solvothermal, high-power ultra-sonication, microwave-assisted thermal treatment, liquid-phase exfoliation, etc. [47]. In addition, according to Figure 6, GQDs have been synthesized by oxidative treatment of graphene oxide using the popular "Hummer's method" (see Figure 6(a)), and sometimes, GQDs have also been made by partial pyrolysis of organic matter such as polythiophene,

citric acid, and sugar (see Figure 6 (b)). Therefore, properties have varied according to techniques of synthesis [48].
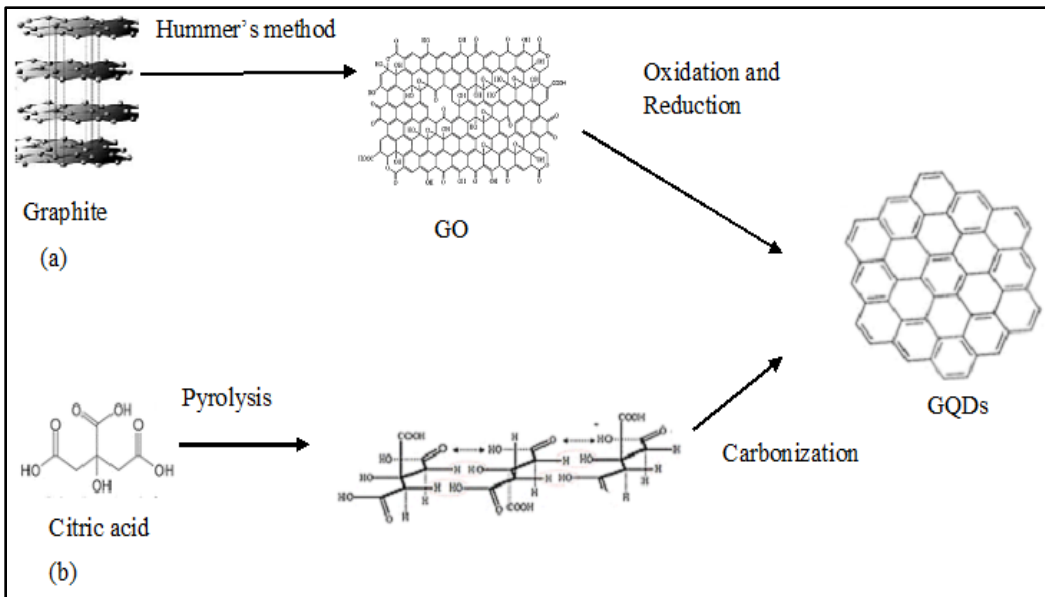
Figure 6. Summary of common methods of synthesis in production of GQDs (a) top-down approach (b) bottom-up approach [48].

Further, GQDs have been utilized for modification of electrode conductivity and as the catalyst for vapor deposition growth [47]. Moreover, GQDs are carbon-based, nanoscale particles that display better, physical, biological and chemical properties and GQDs are widely used in applications of nanomedicine due to its unique electronic structure [42].

Applications of Groups of Graphite Derivatives

There are vast applications of graphite derivatives in different fields, especially electrical and electronic, medical sector, polymer-based manufacturing products, biological field, etc. as shown in Table 4.

Table 4. Applications of graphite derivatives

Graphite derivative	Application(s)	Reference
Graphite	manufacture of carbon brushes in electric motors	[49]
	lubricants for high temperature	[50]
	conductive paint coatings	[51]
Graphene	fuel cell, supercapacitor, hydrogen storage	[52]
	graphene platform for sensing biomolecules	[53]
	electrocatalytic activity	[54]
	field effect transistor	[55]
	corrosion-resistant coating	[56]
GO	surfactant for the emulsification of organic solvents in water	[57]
	electrode materials	[58]
	transparent conductive films (touch screens, liquid crystal displays, organic photovoltaic cells, etc.)	[40]
	gas sensor	[59]
	energy storage device	[60]
EG	electrochemical sensor	[61]
	thermal energy storage device	[62]
rGO	gas sensor	[59]
	biosensors (as semi-conductor)	[63]
	hole transport layer in polymer solar cells and LEDs	[64]
	printable electronic device	[43]
GQD	catalysts for the decomposition of solid composite propellants	[47]
	stabilizing agent	[65]
	bioimaging and biosensing	[42]

Carbon black and Graphene-Derivative-Based Polymer Composites

In the last decade, carbon-based fillers have been highly attracted to industrial interests due to increasing technological perspective of carbon-based fillers in many applications. Reinforcement effect of carbon fillers in polymer composites is related to improvement in failure or mechanical properties and properties such as electrical and thermal conductivity. However, properties of carbon-based filler filled polymer composites significantly vary according to different factors of carbon such as size, geometry, surface area, mixing technique, mixing time, chemical behavior and physical properties [9,66]. Most of the published research studies are based on different forms of carbon filler filled polymer composites for various industrial usages [67, 68, 69]. In a previous study, Kasgoz *et al*. [66] investigated morphological, mechanical and rheological properties of cycloolefin copolymer (COC) composites filled with different types of carbon fillers such as CB, carbon fiber, graphite and expanded graphite (EG) [66]. Results indicated a remarkable improvement of dynamic viscosity for EG and CB filled COC composites. Further, polycarbonate (PC) composites have been prepared in the past with different types of carbon fillers namely, CB, EG, and MWCN [70] and varying the loading of these fillers. A greater improvement of thermal conductivity at 10 mass% of EG filler was recorded. Furthermore, superior thermal conductivity of 1.19 $Wm^{-1}K^{-1}$ has been achieved when the mass ratio of EG: MWCNTs was 9:1. Therefore, these results emphasize that the combination of EG and MWCNTs demonstrated a synergistic effect. Polydimethylsiloxane (PDMS) composites prepared with EG showed significant improvement of thermal conductivity and flexibility [71] and 10 mass% of EG has been selected as the optimum loading.

In addition, thermal and flammability properties of CNT and graphite filled rigid polyurethane composites have been studied and it was found that both CNT and graphite have a minor impact on the decomposition process during thermal degradation of polyurethane [72]. Further,

poly(lactic acid) composites prepared with polyethylene glycol grafted graphene (PEG-g-GN) showed significant improvement of tensile strength and at 1 wt% PEG-g-GN showed the highest property improvement due to the improvement of compatibility between poly(lactic acid) and GN [73]. Moreover, properties of thermally exfoliated and partially reduced GO (TERGO) and GO filled polylactide and polycaprolactone composites have been studied and they have been utilized for thermal management and other packaging applications [74].

Graphite Derivatives-based Natural Rubber Composites

Generally, elasticity and flexibility are the most inherent properties of NR [75] and these properties are very important in different industrial applications, especially for tire and automobile industries. Additives such as graphene derivatives can be added into NR during compounding to improve its performance as well as promote the vulcanization process [76]. However, limited number of studies has been conducted on natural graphite-based NR composites due to their low solubility and poor dispersibility in the NR matrix [42]. Therefore, natural graphite is modified according to different techniques via chemical, mechanical, thermal, etc. to incorporate into NR [42]. In a recent study, Huang *et al.*, [77] synthesized polyethylene glycol grafted graphene (PEG-g-GN) to enhance electrical properties of poly (lactic acid) nanocomposite due to poor adhesion of unmodified natural graphite [77]. Further, mechanical and chemical resistance of GO, rGO and bentonite clay incorporated NR composites [42] have been evaluated and remarkable improvement of tensile strength was found in NR/rGO composite.

Graphite derivatives GO and rGO have been used in bicycle tire production as GO and rGO exhibit numerous advantages such as improved abrasion resistance, decreased rolling resistance of tire, etc. [78]. According to a previous study, GO at 3 phr loading showed significant improvement in physico-mechanical properties of NR compounds as shown in Table 5 [75].

Table 5. Physico-mechanical properties of NR/GO composite

Composite	Tensile strength (MPa)	Modulus at 100% elongation (MPa)	Elongation at break (%)	Hardness (IRHD)	Abrasion volume loss (mm³)	Compression set (%)
NR/GO	32.79	19.51	500.02	71.01	37.45	39.05

Moreover, graphite derivatives are defined as modified graphite, this modified graphite contains some polar groups such as hydroxyl, carboxyl, and epoxide, which make graphene easily functionalized by grafting small molecules [78].

Due to chemical and physical nature of graphite derivatives, stability of aqueous suspensions of these is relatively very low when compared to carbon black, hence it tends to agglomerate. The stability of suspensions of graphite derivatives has been successfully obtained by using surfactants [79]. However, the selection of surfactant is very difficult as it can influence morphology and other chemical and physical properties of composites, even it could affect percolation threshold. However, thermally reduced graphite oxide (TRGO) incorporated NR latex composites have been developed by using two types of surfactants namely ionic sodium dodecyl sulfate (SDS) and non-ionic pluronic F 127 [80]. In addition, composite prepared with 3 phr loading of TRGO has shown a significant improvement in terms of tensile performance and electrical conductivity [80].

Other than that, graphite powder has been utilized as solid lubricating filler due to it is grease-type material. [81]. NR composites prepared with silica and graphite powder as binary filler system showed better mutual dispersion in terms of mechanical and age resistance properties [81]. Properties of NR/GO nanocomposites were scattered, and property improvements shown by the nanocomposites produced via latex pre-compounding compared to those produced via direct melt mixing were attributed to better dispersion of GO layers [82]. In a recent study, NR

composites with vein graphite have been prepared with different vein graphite loadings and high tensile strength was observed at vein graphite loading of 10% [83]. Further, microstructures of GO have been incorporated into NR composites through latex co-coagulation technique [84]. The results showed that highly exfoliated GO sheets were finely dispersed in the NR matrix with strong interface interaction between GO and NR. Tensile strength, tear strength and modulus significantly improved at low loading of GO [84].

NR /Exfoliated GO composites were prepared by a simple and promising latex co-coagulation method [85]. Latex co-coagulation realized the complete exfoliation and uniform dispersion of exfoliated GO in a NR latex matrix. Results revealed that with the increase of the content of exfoliated GO sheet, physico-mechanical properties and fracture initiation highly improved than the traditional fillers [85]. In addition, fatigue crack growth resistance was remarkably enhanced with the incorporation of only 1 phr of exfoliated GO sheet. Further, graphite was coated with different types of chemicals to enhance the performance with NR [86]. NR composites have been prepared with coated graphite using different coating chemicals namely methyl methacrylate, n-butyl acrylate and acrylic acid [86]. Further, the best coating type was achieved with a ratio of 1:1 between methyl methacrylate and n-butyl acrylate [86]. To improve dispersion of EG in NR matrices, surface modified expanded graphite (MEG)/polar compatibilizer namely epoxidized natural rubber (ENR) masterbatches were prepared by solution mixing [87]. Thereafter, the MEG/ENR masterbatches were mixed with NR in the presence and absence of carbon black (CB) [87]. The NR composite prepared with MEG and MEG/CB showed significant improvement of mechanical, thermal and dynamic mechanical properties [87]. Further, physico-mechanical properties and flame-retardant performance of NR composites were developed by using double-shell co-microencapsulated ammonium polyphosphate and EG [88]. Furthermore, NR vulcanizates have been reinforced by carbon

nanotubes (CNT, 3 phr), graphite particles (GP) and CNT/GP hybrid filler (varied GP 0–50 phr) [89]. It was found that a combination of 3 phr CNT and 30 phr GP gives superior properties to NR vulcanizates [89].

EG and hydrogenated NR (HNR) latex composites were prepared with hydrogenation conversions of 60 and 95 mol% (HNR60 and HNR95, respectively) [90]. The results showed that, highest tensile strength, weather resistance, and electromagnetic shielding efficiency of HNR60 were achieved when the amount of dispersed EG was 10% [90]. Other than that, melamine salt of pentaerythritol phosphate/graphite (MPP-G) has been synthesized by dispersing graphite flakes in melamine salt of pentaerythritol phosphate [91]. Thereafter, NR composites were prepared with different loading levels of MPP-G and thermal stability and flammability properties of these composites were studied [91].

According to the above literature, graphite-based materials have been used in different manufacturing applications. Therefore use of the powerful materials, modified graphite or graphite derivatives in rubber composites would lead to a revolution of traditional rubber technology.

Conclusion

Graphite derivatives incorporated rubber composites have been extensively investigated. Incorporation of modified graphite into NR has several advantages such as enhancement of physico-mechanical properties is better than other conventional fillers, excellent electrical and thermal conductivity, gas barrier properties are better than the other additives such as silica, clay, calcium carbonate, etc. Most graphite derivatives appear in solid micro form, hence these cannot be directly incorporated into NR due to environmental effects such as pollution. Therefore, graphite derivatives are mixed with different chemicals or polymers in liquid state such as natural or synthetic latices before incorporating into different types of polymers. However, there are some challenges yet in the research and development of graphite-based rubber composites as some graphite derivatives do not disperse

homogeneously in the rubber matrix and there is a difficulty in understanding the interactions between graphite and rubber in molecular scale. In addition, preparation of rubber/graphene composites by melt mixing is a challenge due to the high viscosity of rubbers, strong tendency of graphene to aggregate, and poor compatibility between graphene and rubber matrix. Not only that, most of the research work has been focused on low loadings of graphite derivative filled polymer systems. However, in most cases, for industrial engineering applications or rubber components such as tires, carpet dampers, etc., the carbon black loading is much higher, even more than 50 or 60 wt%. In such cases, low loading of graphite is not sufficient to compete with carbon black for the above applications. Other than that, graphite derivatives-based applications are limited as poor solubility and low packing density of graphite powder make it difficult to feed into the rubber matrix. Another challenge is to reduce the high cost of graphite derivatives and modified graphite in industrial scale manufacture of graphene-rubber composites. However, graphite-based derivatives could be used to manufacture many kinds of appertinent things. Therefore, it is believed that with more theoretical work, practical research, and technological advances, these challenges would eventually be resolved appropriately in the near future.

Conflict of Interest

The authors declare no conflict of interest.

References

[1]   L. Bokobza. Natural rubber nanocomposites: A review. *Nanomaterials*. **2019**, 9, 12.

[2]   B. Huneau. Strain-induced crystallization of natural rubber: A review of X-ray diffraction investigations. *Rubber Chem. Technol*. **2011**, 84, 425–452.

[3]   C. M. Roland. Reinforcement of elastomers. *Mater. Sci. Eng.* **2016**.

[4]   C. S. Chung. Development of Natural Rubber/Graphene Derivatives-Bentonite Nanocomposites (Doctoral dissertation, UTAR). **2015**.

[5]   A. Kausar, Contemporary applications of carbon black-filled polymer composites: An overview of essential aspects. *J. Plast. Film Sheeting*. **2018**, 34, 256-299.

[6]   M. E. Spahr, R. Rothon. Carbon black as a polymer filler. *Polym. Polym. Compos.* **2017**, 261–291.

[7]   J. C. Bart, Additives in polymers: Industrial analysis and applications. *John Wiley & Sons*. **2005**.

[8]   S. Al-Malaika, F. Axtell, R. Rothon, M. Gilbert. Additives for plastics. In Brydson's Plastics. *Materials*, **2017**, 127-168.

[9]   H. Zhang, H. Zhang, A. Aldalbahi, X. Zuo, C. Fan, X. Mi. Fluorescent biosensors enabled by graphene and graphene oxide. *Biosens. Bioelectron.* **2017**, 89, 96-106.

[10]   R. D. McCullough, R. D. Lowe, M. Jayaraman, D. L. Anderson. Design, synthesis, and control of conducting polymer architectures: structurally homogeneous poly (3-alkylthiophenes). *J. Org. Chem.* **1993**, 58, 904-912.

[11]   S. K. Jebur. Carbon black production, analyzing and characterization (master's thesis). **2018**.

[12]   L. Moulin, S. Da Silva, A. Bounaceur, M. Herblot, Y. Soudais. Assessment of recovered carbon black obtained by waste tires steam water thermolysis: an industrial application. *Waste Biomass Valori.* **2017**, 8, 2757-2770.

[13]   H. Guo, S. Jerrams, Z. Xu, Y. Zhou, L. Jiang, L. Zhang, L. Liu, S. Wen. Enhanced fatigue and durability of carbon black/natural rubber composites reinforced with graphene oxide and carbon nanotubes. *Eng. Fract. Mech.* **2020**, 223, 106764.

[14]   S. Bharech, R. Kumar. A review on the properties and applications of graphene. *J. Mater. Sci. Mech. Eng.* **2015**, 2, 70.

[15]   K. Joshi, M. I. Arefev, L. V. Zhigilei. Generation and characterization of carbon fiber microstructures by atomistic simulations. *Carbon*. **2019**, 152, 396-408.

[16]   H. G. Chae, B. A. Newcomb, P. V. Gulgunje, Y. Liu, K. K. Gupta, M. G. Kamath, K. M. Lyons, S. Ghoshal, C. Pramanik, L. Giannuzzi, K. Şahin. High strength and high modulus carbon fibers. *Carbon*, **2015**, 93, 81-87.

[17]   M. Yu, Y. Xu, C. Wang, X. Hu, B. Zhu, K. Qiao, H. Yuan. Heredity and difference of multiple-scale microstructures in PAN-based carbon fibers and their precursor fibers. *J. Appl. Polym. Sci*, **2012**, 125, 3159-3166.

[18]   T. K. Das, P. Ghosh, N. C. Das. Preparation, development, outcomes, and application versatility of carbon fiber-based polymer composites: a review. *Adv. Compos. Hybrid Mater.* **2019**, 1-20.

[19]   F. Wang, Carbon fibers and their thermal transporting properties. In Thermal Transport in Carbon-Based Nanomaterials, **2017**, 135-184.

[20]   https://www.pdfdrive.com/handbook-of-carbon-graphite-diamond-and-fullerenes-properties-processing-and-applications-volume-in-materials-science-and-process-technology-series-noyes-publications-e183936908.html accessed: 10th of January, **2021**.

[21]   I. Krupa, I. Chodák, Physical properties of thermoplastic/graphite composites. *Eur. Polym. J.* **2001**, 2001, 37, 2159-2168.

[22]   M. J. Mochane, T. E. Motaung, S. V. Motloung, Morphology, flammability, and properties of graphite reinforced polymer composites. Systematic review. *Polym. Compos*. **2018**, 39, E1487-E1499.

[23]   H. O. Pierson. Handbook of carbon, graphite, diamonds and fullerenes: processing, properties and applications. William Andrew, **2012**.

[24]   J. Keeling, Graphite: properties, uses and South Australian resources. *MESA J.* **2017**, 84, 28-41.

[25]   A. D. Jara, A. Betemariam, G. Woldetinsae, J. Y. Kim. Purification, application and current market trend of natural graphite: A review. *Int. J. Min. Sci. Technol*. **2019**, 29, 671-689.

[26]   T. C. Mokhena, M. J. Mochane, S. J. Sefadi, S. V. Motloung, D. M. Andala. Thermal conductivity of graphite-based polymer composites, **2018**, 18.

[27]   P. Ding, S. Su, N. Song, S. Tang, Y. Liu, L. Shi, Highly thermal conductive composites with polyamide-6 covalently-grafted graphene by an in situ polymerization and thermal reduction process. *Carbon*, **2014**, 66, 576-584.

[28]   M. Sohail, M. Saleem, S. Ullah, N. Saeed, A. Afridi, M. Khan, M. Arif, Modified and improved Hummer's synthesis of graphene oxide for capacitors applications. *Mod. Electron. Mater.* **2017**, 3,110-116.

[29]   H. Zhang, C. Peng, J. Yang, M. Lv, R. Liu, D. He, C. Fan, Q. Huang. Uniform ultrasmall graphene oxide nanosheets with low cytotoxicity and high cellular uptake. ACS *Appl. Mater. Interfaces*, **2013**, 5, 1761-1767.

[30]   H. L. Poh, F. Šaněk, A. Ambrosi, G. Zhao, Z. Sofer, M. Pumera. Graphenes prepared by Staudenmaier, Hofmann and Hummers methods with consequent thermal exfoliation exhibit very different electrochemical properties. *Nanoscale*, **2012**, 4, 3515-3522.

[31]   N. Kumar V. C. Srivastava, Simple synthesis of large graphene oxide nano-sheets via electrochemical method coupled with oxidation process. **2019**.

[32]   N. G. Barbakadze, V. G. Tsitsishvili, T. V. Korkia, Z. G. Amiridze, N. V. Jalabadze, R. V. Chedia. Synthesis of graphene oxide and reduced graphene oxide from industrial graphite foil wastes. *Eur. Chem. Bull.* **2018**, 7, 329-333.

[33]   A. K. Kole, S. Biswas, C. S. Tiwary, P. Kumbhakar. A facile synthesis of graphene oxide–ZnS/ZnO nanocomposites and observations of thermal quenching of visible photoluminescence emission and nonlinear optical properties. *J. Lumin*., **2016**, 179, 211-221.

[34]   K. S. Novoselov, A. K. Geim, The rise of graphene. *Nat. Mater*. **2007**, 6, 183-191.

[35]   X. Zhang, L. Shen, X. Xia, H. Wang, Q. Du. Study on the interface of phenolic resin/expanded graphite composites prepared via in situ polymerization. *Mater. Chem. Phys.* **2008**, 111, 368-374.

[36]   G. Chen, W. Weng, D. Wu, C. Wu. PMMA/graphite nanosheets composite and its conducting properties. *Eur. Polym. J.* **2003**, 39, 2329-2335.

[37]   A. Karaipekli, A. Biçer, A. Sarı, V. V. Tyagi. Thermal characteristics of expanded perlite/paraffin composite phase change material with enhanced thermal conductivity using carbon nanotubes. *Energy Convers. Manag.* **2017**, 134, 373-381.

[38]   B. Zhang, Y. Tian, X. Jin, T. Y. Lo, H. Cui. Thermal and mechanical properties of expanded graphite/paraffin gypsum-based composite material reinforced by carbon fiber. *Materials*, **2018**, 11, 2205.

[39]   G. Williams, B. Seger, P. V. Kamat. TiO_2-graphene nanocomposites. UV-assisted photocatalytic reduction of graphene oxide. *ACS Nano*, **2008**, 2, 1487-1491.

[40]   Q. Zheng, Z. Li, J. Yang, J. K. Kim. Graphene oxide-based transparent conductive films. *Prog. Mater. Sci*, 2014, 64, 200-247.

[41]   S. Pei, H. M. Cheng. The reduction of graphene oxide. *Carbon*, **2012**, 50, 3210-3228.

[42]   S. Chung, R.A. Revia, M. Zhang. Graphene quantum dots and their applications in bioimaging, biosensing, and therapy. *Adv. Mater*. **2019**, 1904362.

[43]   Y. Zhu, S. Murali, W. Cai, X. Li, J. W. Suk, J. R. Potts, R. S. Ruoff. Graphene and graphene oxide: synthesis, properties, and applications. *Adv. Mater*. **2010**, 22, 3906-3924.

[44]   E. Jaafar, M. Kashif, S. K. Sahari, Z. Ngaini, Study on morphological, optical and electrical properties of graphene oxide (GO) and reduced graphene oxide (rGO). *Mater. Sci. Forum*, **2018**, 917, 112-116.

[45]   A. H. Tarekegne, D. A. Worku. Synthesis and Characterization of Reduced Graphene Oxide (rGO) Started from Graphene Oxide (GO) Using the Tour Method with Different Parameters. *Adv. Mater. Sci. Eng*., **2019**, 2019, 5058163.

[46]   A. T. Smith, A. M. LaChance, S. Zeng, B. Liu, L. Sun. Synthesis, properties, and applications of graphene oxide/reduced graphene oxide and their nanocomposites. *Nano Mater. Sci.* **2019**, 1, 31-47.

[47]   J. P. Melo, P. L. Ríos, P. Povea, C. Morales-Verdejo, M. B. Camarada. Graphene oxide quantum dots as the support for the synthesis of gold nanoparticles and their applications as new catalysts for the decomposition of composite solid propellants. *ACS omega*, **2018**, 3, 7278-7287.

[48]   K. L Schroeder, R. V. Goreham, T. Nann. Graphene quantum dots for theranostics and bioimaging. *Pharm. Res.* **2016**, 33, 2337-2357.

[49]   H. Kobayashi, Aisin Seiki Co Ltd, 2010. Method of manufacturing metal-graphite brush material for motor. U.S. Patent 7,767,113.

[50]   W. Huai, C. Zhang, S. Wen. Graphite-based solid lubricant for high-temperature lubrication. Friction, **2020**, 1-13.

[51]   S.S. Azim, A. Satheesh, K.K. Ramu, S. Ramu, G. Venkatachari. Studies on graphite based conductive paint coatings. *Prog. Org. Coat.* **2006**, 55(1), 1-4.

[52]   C. Liu, S. Alwarappan, Z. Chen, X. Kong, and C.Z. Li, Membraneless enzymatic biofuel cells based on graphene nanosheets. *Biosens Bioelectron.* **2010**, 25, 1829-1833.

[53]   C. H. Lu, H. H. Yang, C. L. Zhu, X. Chen, G. N. Chen. A graphene platform for sensing biomolecules. *Angew. Chem.* **2009**, 121, 4879-4881.

[54]   L. Qu, Y. Liu, J. B. Baek, L. Dai. Nitrogen-doped graphene as efficient metal-free electrocatalyst for oxygen reduction in fuel cells. *ACS nano*, **2010**, 4, 1321-1326.

[55]   C. Y. Su, Y. Xu, W. Zhang, J. Zhao, A. Liu, X. Tang, C. H. Tsai, Y. Huang, L. J. Li. Highly efficient restoration of graphitic structure in graphene oxide using alcohol vapors. *ACS Nano*, **2010**, 4, 5285-5292.

[56]   S. Somnath, A. Belianinov, S. V. Kalinin, S. Jesse. Full information acquisition in piezoresponse force microscopy. *Appl. Phys. Lett.* **2015**, 107, 263102.

[57]   D. P. Hansora, N. G. Shimpi, S. Mishra. Graphite to graphene via graphene oxide: an overview on synthesis, properties, and applications. *Jom*, **2015**, 67, 2855-2868.

[58]   Y. Zhu, D. K. James, J. M. Tour. New routes to graphene, graphene oxide and their related applications. *Adv. Mater.* **2012**, 24, 4924-4955.

[59]   S. Drewniak, R. Muzyka, A. Stolarczyk, T. Pustelny, M. Kotyczka-Morańska, M. Setkiewicz, Studies of reduced graphene oxide and graphite oxide in the aspect of their possible application in gas sensors. *Sensors,* **2016**, 16, 103.

[60]   M. A. Pope, C. Punckt, I. A. Aksay, Intrinsic capacitance and redox activity of functionalized graphene sheets. *J. Phys. Chem. C*, **2011**, 115, 20326-20334.

[61]   S. J. Rowley-Neale, E. P. Randviir, A. S. A. Dena, C. E. Banks. An overview of recent applications of reduced graphene oxide as a basis of electroanalytical sensing platforms. *Appl. Mater. Today*, **2018**, 10, 218-226.

[62] B. Zhang, Y. Tian, X. Jin, T. Y. Lo, H. Cui. Thermal and mechanical properties of expanded graphite/paraffin gypsum-based composite material reinforced by carbon fiber. *Materials*, **2018**, 11(11), 2205.

[63] Q. He, S. Wu, S. Gao, X. Cao, Z. Yin, H. Li, P. Chen, H. Zhang. Transparent, flexible, all-reduced graphene oxide thin film transistors. *ACS Nano*, **2011**, 5, 5038-5044.

[64] S. K. Saha, S. Bhaumik, T. Maji, T. K. Mandal, A. J. Pal. Solution-processed reduced graphene oxide in light-emitting diodes and photovoltaic devices with the same pair of active materials. *RSC Advances*, **2014**, 4, 35493-35499.

[65] Y. Li, N. Chopra, Gold nanoparticle integrated with nanostructured carbon and quantum dots: synthesis and optical properties. *Gold Bull.* **2015**, 48, 73-83.

[66] A. Kasgoz, D. Akın, A. L. Ayten, A. Durmus. Effect of different types of carbon fillers on mechanical and rheological properties of cyclic olefin copolymer (COC) composites. *Compos. B. Eng.* **2014**, 66, 126-135.

[67] K. P. Sau, T. K. Chaki, D. Khastgir, The change in conductivity of a rubber-carbon black composite subjected to different modes of pre-strain. Composites Part A: *Appl. Sci. Manuf. Compos.*, **1998**, 29, 363-370.

[68] N. A. Mohd Radzuan, A. B. Sulong, M. Rao Somalu, E. H. Majlan, T. Husaini, M. I. Rosli. Effects of die configuration on the electrical conductivity of polypropylene reinforced milled carbon fibers: An application on a bipolar plate. *Polymers*, **2018**, 10, 558.

[69] K. T. S. Kong, M. Mariatti, A. A. Rashid, J. J. C. Busfield. Enhanced conductivity behavior of polydimethylsiloxane (PDMS) hybrid composites containing exfoliated graphite nanoplatelets and carbon nanotubes. *Composites Part B: Engineering*, **2014**, 58, 457-462.

[70] F. Zhang, Q. Li, Y. Liu, S. Zhang, C. Wu, W. Guo. Improved thermal conductivity of polycarbonate composites filled with hybrid exfoliated graphite/multi-walled carbon nanotube fillers, *J. Therm. Anal. Calorim.* **2016**, 123, 431-437.

[71] W. Zeng, X. M. Tao, S. Lin, C. Lee, D. Shi, K. H. Lam, B. Huang, Q. Wang, Y. Zhao, Defect-engineered reduced graphene oxide sheets with high electric conductivity and controlled thermal conductivity for soft and flexible wearable thermoelectric generators. *Nano Energy*, **2018**, 54, 163-174.

[72] E. Ciecierska, M. Jurczyk-Kowalska, P. Bazarnik, M. Kowalski, S. Krauze, M. Lewandowska. The influence of carbon fillers on the thermal properties of polyurethane foam. *J. Therm. Anal. Calorim.* **2016**, 123, 283-291

[73] K. Huang, H. Yu, M. Xie, S. Liu, and F. Wu. Effects of poly (ethylene glycol)-grafted graphene on the electrical properties of poly (lactic acid) nanocomposites. *RSC Advances*, **2019**, 9,10599-10605.

[74] O. J. Botlhoko, J. Ramontja, S. S. Ray. Thermally shocked graphene oxide-containing biocomposite for thermal management applications. *RSC Advances*, **2017**, 7, 33751-33756.

[75] L. O. Ekebafe, G. O. Adebayo, M. N. Chukwu, K. O. Eguare, Performance evaluation of graphite oxide in natural rubber compounds. *Nigerian J. Chem. Res.* **2019**, 24, 20-33.

[76] M. Groover. Fundamentals of modern manufacturing. Hoboken, NJ: J. *Wiley & Sons,* **2010**, 177, 178

[77] K. Huang, H. Yu, M. Xie, S. Liu, F. Wu. Effects of poly (ethylene glycol)-grafted graphene on the electrical properties of poly (lactic acid) nanocomposites. *RSC Advances*, **2019**, 9, 10599-10605.

[78]   J. Wang, K. Zhang, Q. Bu, M. Lavorgna, H. Xia. Graphene-rubber nanocomposites: preparation, structure, and properties. In Carbon-related materials in recognition of nobel lectures by Prof. Akira Suzuki in ICCE, 2017, 175-209.

[79]   E. E. Tkalya, M. Ghislandi, G. de With, C. E. Koning, The use of surfactants for dispersing carbon nanotubes and graphene to make conductive nanocomposites. *Curr. Opin. Colloid Interface Sci.* **2012**, 17, 225-232.

[80]   H. Aguilar-Bolados, J. Brasero, M. A. López-Manchado, M. Yazdani-Pedram. High performance natural rubber/thermally reduced graphite oxide nanocomposites by latex technology. *Compos. Part B: Eng.* **2014**, 67, 449-454.

[81]   M. N. Alam, V. Kumar, P. Potiyaraj, D. J. Lee, J. Choi. Mutual dispersion of graphite–silica binary fillers and its effects on curing, mechanical, and aging properties of natural rubber composites. *Polym. Bull.* **2021**, 1-18.

[82]   P. Berki, K. László, N. T. Tung, J. Karger-Kocsis. Natural rubber/graphene oxide nanocomposites via melt and latex compounding: Comparison at very low graphene oxide content. *J. Reinf. Plast. Compos*. **2017**, 36, 808-817.

[83]   M. P. Viyanage, T. R. T. Manage, R. C. L. de Silva, L. C. D. Nayanajith, M. Y. D. Milani, I. R. M. Kottegoda, Mechanical property evaluation of natural rubber/vein graphite composites. *Sri Lankan J. Phys.,* **2021**, 22, 29.

[84]   Y. Mao, C. Wang, L. Liu. Preparation of graphene oxide/natural rubber composites by latex co-coagulation: Relationship between microstructure and reinforcement. *Chin. J. Chem. Eng*. **2020**, 28, 1187-1193.

[85]   B. Dong, C. Liu, L. Zhang, Y. Wu. Preparation, fracture, and fatigue of exfoliated graphene oxide/natural rubber composites. *RSC Advances*, **2015**, 5, 17140-17148.

[86]   J. Song, L. Ma, Y. He, H. Yan, Z. Wu, W. Li. Modified graphite filled natural rubber composites with good thermal conductivity. *Chin. J. Chem. Eng*. **2015**, 23, .853-859.

[87]   A. Malas, C.K. Das, A. Das, G. Heinrich. Development of expanded graphite filled natural rubber vulcanizates in presence and absence of carbon black: Mechanical, thermal and morphological properties. *Mater. Des*, **2012**, 39, 410-417.

[88]   N. Wang, G. Xu, Y. Wu, J. Zhang, L. Hu, H. Luan, Q. Fang. The influence of expandable graphite on double-layered microcapsules in intumescent flame-retardant natural rubber composites. *J. Therm. Anal. Calorim.* **2016**, 123, 1239-1251.

[89]   W. Kitisavetjit, Y. Nakaramontri, S. Pichaiyut, S. Wisunthorn, C. Nakason, S. Kiatkamjornwong. Influences of carbon nanotubes and graphite hybrid filler on properties of natural rubber nanocomposites. *Polym. Test*, **2021**, 93, 106981.

[90]   T. H. Nguyen, V. A. Nguyen, T. Ougizawa, S. Kawahara, H. H. Cao. Electromagnetic shielding material based on hydrogenated natural rubber/expanded graphite blend: Preparation and characterization. *Polym. Adv. Technol.* **2021**.

[91]   A. Abdelkhalik, G. Makhlouf, A. Abdel-Hakim. Fire Behavior of Natural Rubber Filled with Intumescent Flame Retardant Containing Graphite. *J. Vinyl Addit. Technol.* **2020**, 26, 155-164.