Chapter

Graphene-Like Nanocomposites

Zahra Rafiei-Sarmazdeh and Seyed Javad Ahmadi

Abstract

After discovering graphene and its extraordinary intrinsic, other graphene-like nanomaterials (GLNs) became a topic of interest to many scientists of the time. Recently, GLNs, nanosheets of sp^2-hybridized atoms arranged in a two-dimensional lattice with impressive thermal, mechanical, and electrical properties, has attracted both academic and industrial interest because it can produce dramatic improvements in properties at very low filler content. Many studies have been performed on GLNs with various applications, including boron nitride nanosheets, transition metal dichalcogenides, and other two-dimensional (2D) nanomaterials. This rapid advance provides a strong appetence for further research on properties of GLNs, including mechanical, electrical and thermal properties and their potential applications in the nanocomposites industry.

Keywords: graphene-like, nanocomposite, boron nitride, two-dimensional, nanomaterials, polymer

1. Introduction

Composite is a combination of at least two components (or phases) that are chemically distinctly different, and these components are not dissolvable. Properties and performance of composites strongly depend on their components. In general, in the composite, there is at least one non-interconnected component, called filler or reinforcement, surrounded by a continuous phase, called matrix [1].

Recently, nanocomposites have attracted a lot of attention. Nanocomposite is actually a composite that at least one of its constituents, typically filler, is in dimensions ranging from 1 to 100 nm. The nanomaterials are incorporated within the matrix for particular purposes such as strength, resistance, electrical conductivity, magnetic properties etc.

A great effort is being made to control nanoscale structures through new approaches. The physical, chemical, and biological properties of nanomaterials are different from the properties of atoms and molecules or even bulk materials. However, the properties of nanocomposites depend not only on the properties of filler and matrix, but also on the morphological and interfacial characteristics of these materials. Nanomaterials have a high surface-to-volume ratio, which makes them ideal for use in nanocomposite materials [2].

There are several categories for composite and nanocomposite classification. One of these categories is based on the type of matrix material. On this basis, there are various composites including [3, 4]:

- Polymer matrix composites (PMCs): In commercial applications, these composites have a high rating compared to other types of composites. Various filler materials can be used in this type of composite. The matrix can be made of thermo-plastic and thermo-set polymers.

- Metal matrix composites (MMCs): This category, which is considered an advanced building material, consists of non-metal fillers in a metal matrix. MMCs are mainly used in engineering applications, in cases where the operating temperature is in the range of 250–750°C. Copper, aluminum, titanium and super alloys are widely used to make these composites.

- Ceramic matrix composites (CMCs): This category is considered an advanced building material made of metal/non-metallic fillers in a ceramic matrix. CMCs are used in engineering applications with the operating temperature is in the range of 800–1650°C.

The use of polymer composites due to its inherent properties has grown considerably compared to other composites. High strength and modulus, fatigue resistance, high flexibility, multi-functional performance, easy to process, low weight of structure and low cost processing are the features of this category of composites than other composites.

In recent years, two-dimensional (2D) nanomaterials have drawn considerable interest for exploring potential applications. 2D nanomaterials are laminated crystals that exhibit unusual physical-chemical properties in thicknesses of atomic layers (**Figure 1**). Graphene as a famous member of the family of 2D nanomaterial is a honeycomb network of carbon atoms, co-located with sp^2 hybridize and forming a single graphene atomic layer [5, 6]. Graphene is indubitably one of the most important nanomaterials in the world, which the combination of unique properties in it makes a long way to discover a wide range of applications from

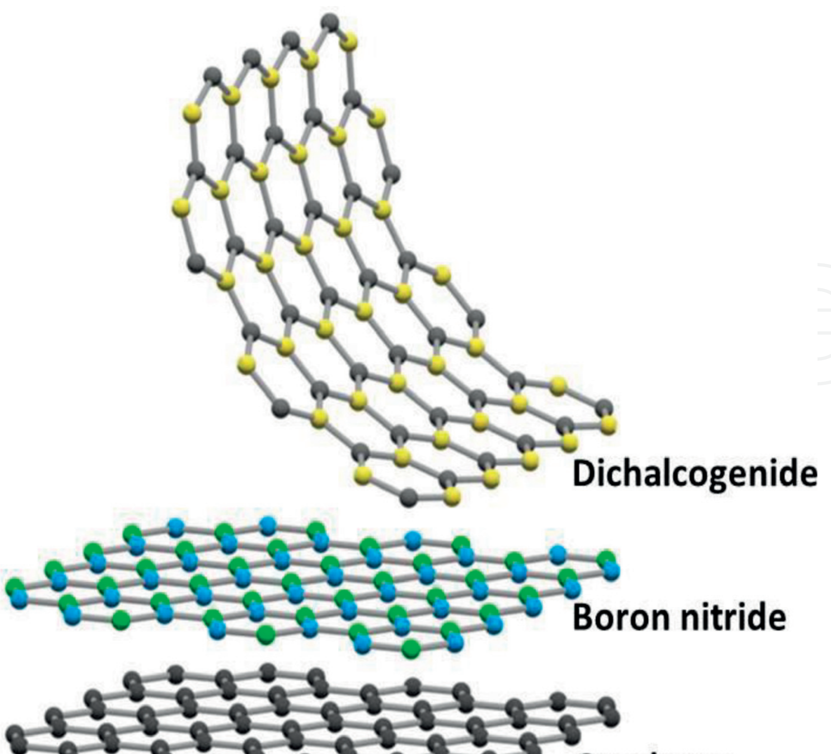

Figure 1.
Schematic view of 2D nanomaterials, a single layer of graphene, boron nitride and transition metal dichalcogenide [15].

electronics to optics [7, 8], sensors [9, 10], biology [11], coating, composite [12, 13] and etc.

Since 2004, when a single layer graphene was discovered by Novoselov [14], for the first time, various studies were carried out on a variety of graphene-like nanomaterials (GLNs), their properties and application. One of the most important uses of GLNs is the usage as filler in polymer composites due to their unique mechanical, electrical and thermal properties.

The scientists and researchers are encouraged to use other 2D nanomaterials such as boron nitride nanosheets (BNNSs) and metal dichalcogenide nanosheets for producing nanocomposite when observed amazing properties of graphene as reinforcement material for polymer-based composites. Generally, 2D nanomaterials have unique properties for using as reinforcement in nanocomposites, which include: (i) ultrathin 2D nanosheets have high special surface area, (ii) they have high surface-to-volume atomic ratio, therefore are chemically suitable for functionalizing and so their dispersion improves in polymer matrix. (iii) They have unique mechanical, thermal and electrical characteristics, which make them an ideal candidate for reinforcement of nanocomposites [16].

In comparison to the zero-dimensional (0D) nanomaterials such as BN nanoparticles or one-dimensional (1D) nanomaterials, such as boron nitride nanotubes (BNNTs), due to the special structure of 2D nanomaterials, contacting or overlapping nanosheets with each other throughout polymeric matrix could form an interconnected network of 2D layers. As a result, the percolation threshold of 2D nanocomposite is lower than other nanocomposites. This means that better properties can be achieved at much lower amounts of reinforcement, which decreases the cost of composite construction.

The other important advantage of the 2D nanosheets is their high surface area, which allows for the proper interaction of filler with polymeric matrix. This interaction results in a dramatic improvement in the properties of the matrix. However, the mentioned properties could be diminished, if the filler is not suitably dispersed or the conditions are created to allow the particles to agglomerate together during the nanocomposite manufacturing. The van der Waals force (vdW) between the layers can lead to agglomeration of nanosheets, which has a negative effect on the properties. On an industrial scale, maintaining the cost of competitive production with a high degree of dispersion and low content of filler is the goal, and therefore the manufacturing processes of these nanocomposites with unique properties that have the capacity to scale up is very valuable.

GLNs are instant and important nanomaterials that have outlandish mechanical and functional properties. Due to their extraordinary properties, these materials have the potential to be recognized as generations of next generation composites with maximum structural and/or functional reinforcement in a minimum amount of filler. Adding these nanomaterials significantly improves the mechanical properties of the polymer matrix. Thermal, electrical conductivity and dimensional stability of nanocomposite significantly change. In addition, the unique properties of each of these nanosheets will appear in the final nanocomposite.

However, the research on GLNs polymer-based nanocomposites is still in its early stages. Little research has been done on the properties of these nanocomposites, such as optical properties, irradiation properties and biocompatibility. The reason is not that these studies are not important or interesting, but rather, the production of GLNs nanocomposite is difficult due to low-yield and high-cost methods to synthesis of GLNs. This prevents the rapid progress of research on properties and application of GLNs polymer-based nanocomposites.

In this chapter, we focus on a summary of recent developments in 2D graphene-like nanomaterials in the manufacture of polymer nanocomposites. We have also reviewed the synthesis methods of GLNs and the processing polymer-based nanocomposites. Some applications of these nanomaterials have been investigated. Ultimately, we have studied the problems and limitations facing this category of nanocomposites.

2. Synthesis approach of graphene-like nanomaterials

2D nanosheets are synthesized using a variety of methods based on two top-down and bottom-up approaches. In top-down approach, the bulk of the parent material is used and the final 2D nanosheets are produced during the processes. This approach can be cost-effective depending on the material used. In this view, 2D nanomaterials are produced by methods such as separation, peeling, cleavage and exfoliation. Micromechanical cleavage, ball milling, liquid/chemical exfoliation and functionalization (covalent and non-covalent) are common methods in this category [17–25].

In the bottom-up, the precursor materials are used for producing of GLNs, with methods such as chemical synthesis, chemical vapor deposition (CVD) and plasma-enhanced chemical vapor deposition (PECVD). However, there are the main challenges facing researchers in this field. One of them is the need for high amounts of nanomaterials and low yield synthesis methods of these nanomaterials. A great effort is being made for improvement the efficiency of the synthesis of these nanosheets [26–28].

In general, interfacial interaction is believed to play an important role in determining the final properties of polymer nanocomposites. Interfacial interaction between the polymer matrix and the filler materials includes van der Waals interactions, hydrous bonds, covalent bonds, and ionic bonds [29]. Hence, many efforts have been made to develop and improve interfacial interactions of nanocomposites including filler or matrix. The functionalization of the filler surface and the use of compatibilizer are common to be modified the surface of filler in terms of polar/nonpolar nature and to be able to interact with the polymeric matrix due to the hydrophobic/hydrophilic nature of polymers used in the composite and coating industry.

3. Graphene-like nanocomposites and their importance

Due to inherent and impressive properties of mechanical, electronic and thermal conductivity of GLNs, these compounds are considered as a promising candidate for using in polymer nanocomposites as fillers. Compared to conventional composites, these nanocomposites show a dramatic increase in properties, even in a low content of filler. Hence, the 2D nanomaterials and GLNs based-nanocomposites are not only lighter, but also have more and stronger multi-functional properties. As mentioned in the previous section, due to the high surface area of GLNs, the physicochemical interaction of the filler with the polymeric matrix enhances. This helps strengthen and enhancement of interfacial bonding between layers of GLNs and polymer matrix [30].

According to the interaction between filler and polymer matrix, polymer composites are divided into three groups; conventional or immiscible composites, intercalated composites, and exfoliated or miscible composites (**Figure 2**). In conventional composites, 2D nanosheets remain as agglomerates in the polymer matrix and retain their original structure. The diffraction pattern of conventional composites is the same as that for the first powder of these nanosheets. In intercalated

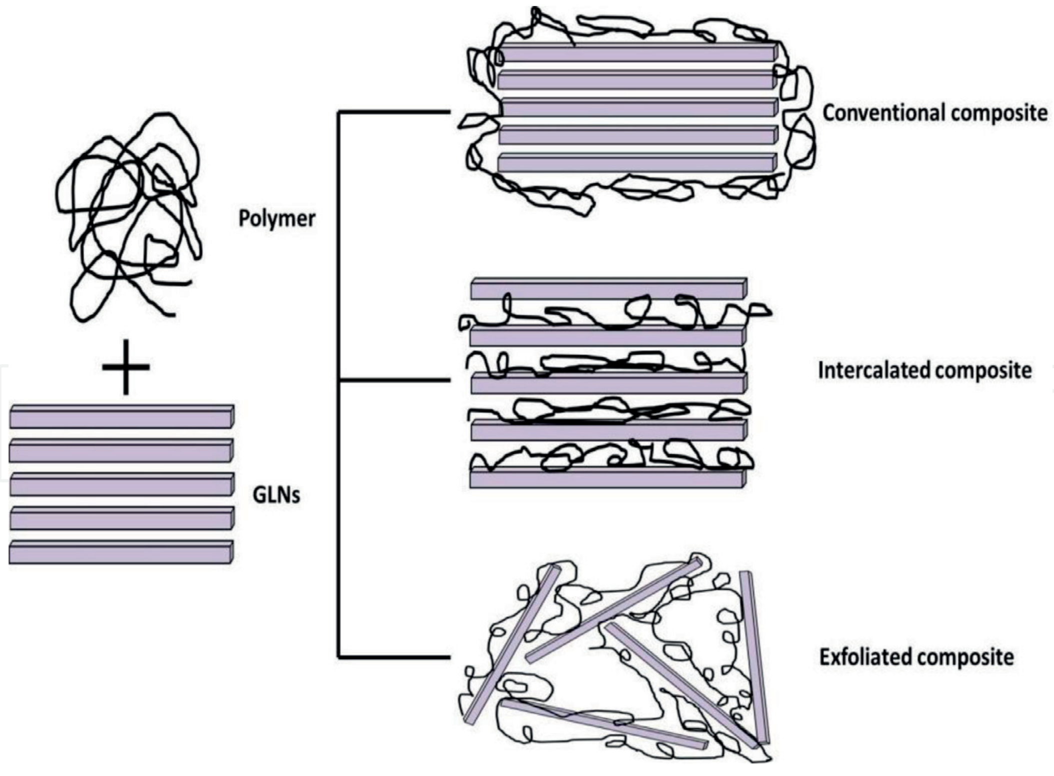

Figure 2.
Schematic view of different groups of composites; conventional, intercalated and exfoliated nanocomposites.

nanocomposites, polymer chains are intercalated between 2D layers, which partially open the layers. The characteristic peak displacement of these nanosheets to lower angles represents intercalating. In the third group, the suitable interaction between filler and the polymer matrix leads to the complete exfoliation of the layers by the polymer chains. The characteristic peak related to these nanosheets disappears in the diffraction pattern of these nanocomposites. In practice, however, it is rarely possible to achieve complete exfoliation [31, 32].

4. Processing

The final properties of nanocomposites depend on the method and processing conditions. Most polymer composites are processed using the following methods: (i) melt processing (ii) solvent processing (iii) *In-situ* polymerization; (iv) electrospinning and (v) layer by layer (LBL) assembly (**Figure 3**).

The melt mixing method is one of the most economical and environmentally friendly methods used to make nanocomposites. In fact, this process is the choice of most industries. The mixing of materials is often done through a single or double extruder, in such a way that the reinforcement is mixed with the molten polymer. The mixer uses shear force to separate the filler agglomerates and disperse them throughout the polymeric matrix (**Figure 3(a)**). Another point of this method is the lack of any solvent for processing. Most polymers used in this method include low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP), polystyrene (PS), poly(methyl methacrylate) (PMMA), polyamide polyester and polycarbonate [30, 33–37].

Solution mixing is another way of producing nanocomposites containing GLNs. In this method, the nanomaterials and polymers are dissolved in the solvent before being molded and then the solvent is evaporated (**Figure 3(b)**). In this method, both thermoset and thermoplastic polymers can be used. Polymers such as PMMA,

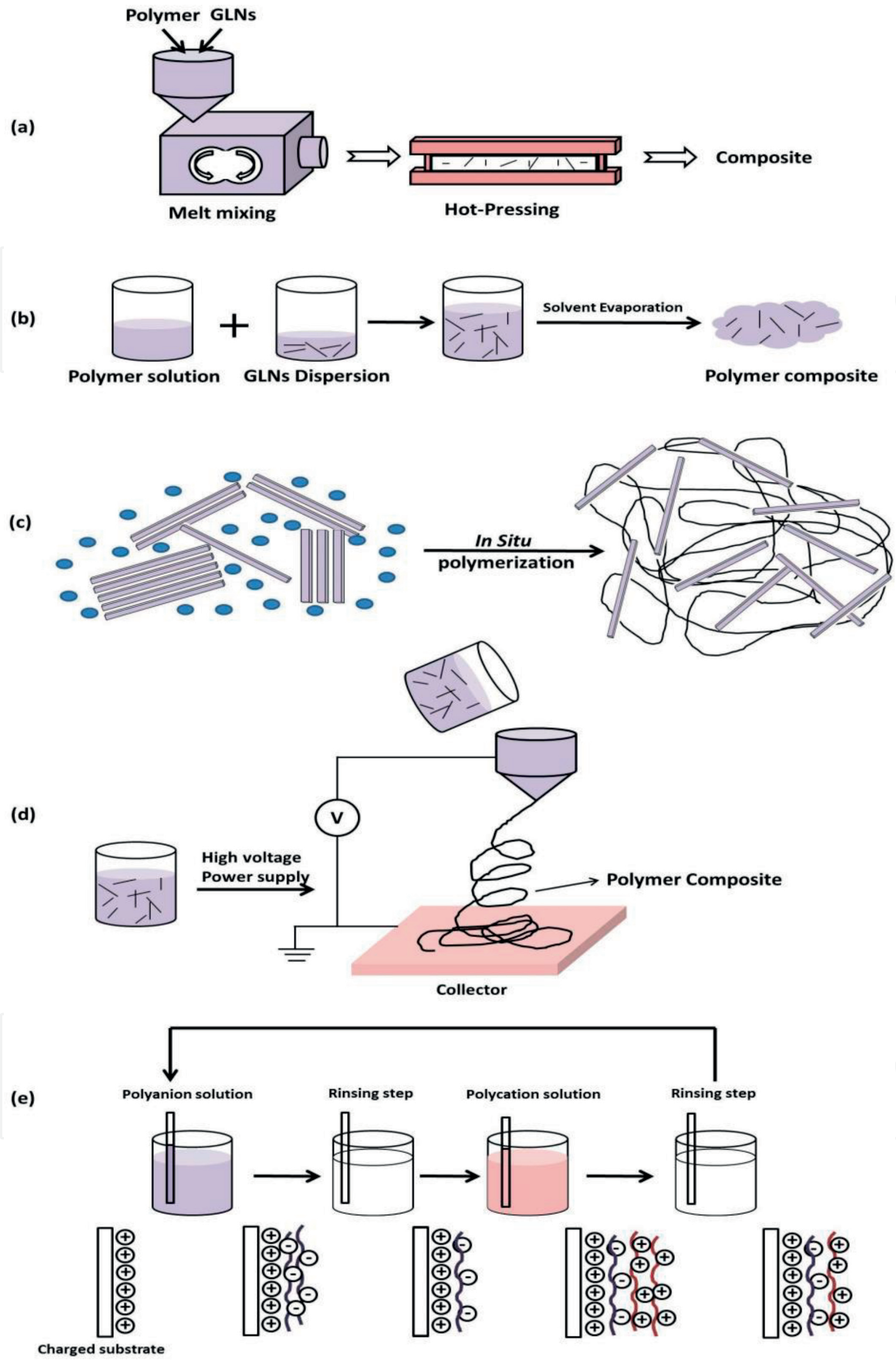

Figure 3.
Schematic image of basic set-up of processing methods of composites (a) melt processing, (b) solvent processing, (c) in-situ *polymerization, (d) electrospinning and (e) layer by layer (LBL) assembly.*

polyvinyl alcohol, poly(hydroxy amino ether), PS, polyethylene (PE), polyethylene oxide (PEO) and epoxy can be used. Low viscosity of polymer in the solution (contrary to the molten method) with mechanical stirring or ultrasonic waves can help the better dispersity of nanosheets in the polymeric matrix [16]. Different solvents can be put in this category such as chloroform, acetonitrile and toluene [38–40].

Another technique is *in situ* polymerization that both thermoset and thermoplastic polymers can be used. The filler should be dispersed in the monomer that is supposed to polymerize (**Figure 3(c)**). Polymerization begins with the use of a chemical that initiates the reaction or the mixing of the two monomers or with the help of temperature. One of the advantages of this method is the ability to graft polymer molecules to the filler surface and better dispersion of nanosheets. This technique can be used to make polymer composites that are not soluble in common solvents or are thermally unstable (for melt mixing). This method has been used in the development of PE [41], PP [42], PMMA [43], nylon 6 [44], PU [45], polylactic acid (PLA) [46], etc. composites.

Another method used to make this type of nanocomposite is electrospinning, which has been reported with the use of polymers such as polyimide, polyurethane (PU) [47], poly(vinyl alcohol) (PVA) [48], gelatin [49], nylon 6 [50], polyaniline (PANI) [51]. In this method, nanosheets orientation is possible along the axis of the fibers (**Figure 3(d)**). Electrospun diameter of polymer fibers can be controlled in the range of tens of nanometers to several micrometers [16].

Another possible way to achieve the proper dispersion of GL nanosheets in the polymeric matrix is layer by layer (LBL) assembly while to maintain the unique properties of the components (**Figure 3(e)**). This technique is obtained by sequential absorption of the charged components in opposite direction by attractive forces such as electrostatic, hydrogen bonding, etc. Therefore, multi-layer structures using the LBL assembly can be manufactured reproducibly, so that it is possible to control the thickness and composition of hybrid nanocomposite at the nanoscale level [52].

Despite the successful use of various methods in the synthesis of these nanocomposites, there is still a lack of information about: (1) the use of a suitable method for a particular compound of a matrix and reinforcement; (2) the maximum reinforcement content for achieving an optimal combination of properties and the low costs [16]. Therefore, it is still necessary to use the simulation and modeling method to achieve the answer to these unbeknownst.

5. Application of graphene-like nanocomposite

Depending on the type of GLNs and its inherent properties, the designed properties of nanocomposite can be received. Extraordinary properties of GLNs, such as BNNSs, including high thermal properties, structural stability, good mechanical properties, and antioxidant ability, have attracted the attention of researchers to use as a filler [53, 54]. A summary of the application of GLNs nanocomposites is shown in **Figure 4**.

Fillers with a high aspect ratio and crystallinity can improve thermal conductivity and reduce Kapitza resistance [55, 56]. For example, most thermoplastic polymers, such as polyethylene, polypropylene, polyamide and thermosets such as epoxy, are insulating and have very low thermal conductivity, but these properties can be improved by adding fillers such as boron nitride. The use of BN in insulating polymer matrix is the solution if both of electrical properties and thermal conductivity are needed in an electronic device [57]. So far, few studies have been carried out on the thermal conductivity of thermoplastics filled with 2D boron nitride [58–65]. Therefore, researchers focus the investigation on the effect of filler (chemical composition, morphology, surface characteristics, shape and size) on electrical conductivity.

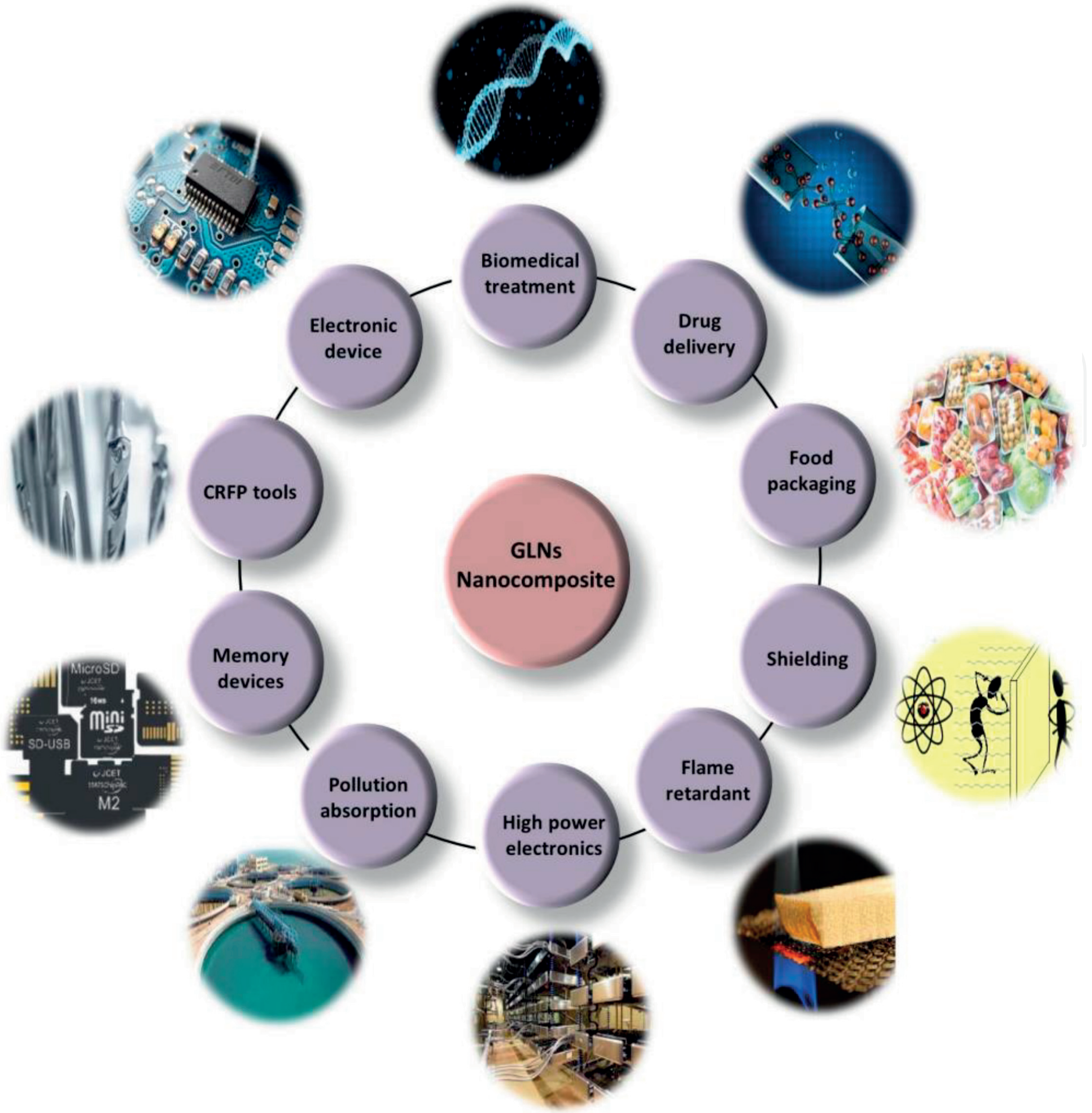

Figure 4.
A summary of the application of GLNs nanocomposites.

The application of epoxy as a thermoset polymer is highly sought-after due to high chemical resistance, corrosion and significant mechanical properties. However, due to very low thermal conductivity (0.15–0.35 W/mK), its use in electronic tools and carbon fiber reinforced plastic (CFRP) tooling is limited. Hence, researchers have used BNNSs to improve the thermal conductivity of this polymer [66, 67].

PVA/BNNSs can be used to make memory devices, due to the huge potential of trapping charge carriers and to perceive the non-volatile memory effect. In these devices, a thin film of hybrid nanocomposite is used as a sandwiched active layer between two conductive electrodes to form the memristor structure [68].

Flexible insulation nanocomposites such as PU/BN nanocomposites show high thermal conductivity that are a desirable option for miniaturization of high-power electronics and portable devices [69].

Polymer materials are widely used in most important industries. However, these materials are high-risk materials to burn, and most of them are decomposed with the emission of toxic gases. Therefore, nanocomposite modification is necessary to reduce their flammability. There are three common strategies to achieve this: the use of inherently flame resistant polymers, flame retardant materials and surface/coating modifications. Usually, a small amount of filler can improve the thermal properties of the nanocomposite. 2D graphene-like nanomaterials as inorganic fillers, if they are well spread on the polymer matrix, can create a physical barrier inside the polymer and prevent the penetration of heat and degradation of polymeric materials. Totally, the addition of 2D nanosheets results in the thermal stability of polymers. This effect can be due to the thermal stability of filler and the barrier effect of these nanomaterials, which leads to the resistance of the nanocomposite to thermal degradation and prevents the penetration of degradation products from the polymer matrix to the gas phase. Several studies have been carried out on the effects of these nanomaterials on the thermal stability of various polymers [61, 70].

GL nanomaterials are capable of separating, organic pollution absorption, water and wastewater treatment, contaminant elimination from oil, due to the nanosheet structure, the polarity of bonds and the high surface area. In practical application and in different situations, these nanosheets due to their powdery state and the ease of collection after separation require for the embedding in a substrate. Therefore, polymer-based nanocomposites of GLNs such as polyvinylidene fluoride (PVDF) (due to high chemical resistance) are used [71–73].

One of the special applications of BNNSs is the neutron shielding property, due to intrinsic property of boron in absorbing neutrons. The placement of boron nitride in a polymeric matrix can produce a multifunctional nanocomposite that exhibits structural, radiation protection, and even resistance to flame. These polymer nanocomposites can be used in spacecraft and nuclear reactors. NASA has focused on the protective properties of nanocomposites containing BNNSs in a polyethylene matrix [74, 75].

Since graphene and graphene oxide have been successfully used in biomedical applications, much attention has been paid to GLNs due to their 2D structure, which is similar to graphene. Polymers, on the other hand, were used in bio-detecting research because of low weight, ease of fabrication, and relatively low cost of processing. The simultaneous use of 2D materials and polymers offers a lot of potential to the researchers. BN has a high biocompatibility due to its excellent chemical stability, good process—ability and good biology activity [76]. For example, chitosan/BN nanocomposites have been used as protective coating for stainless steel. Also, BN is used to strengthen polypropylene as a bio-composite for bone prosthesis [77].

The water-soluble polymers have a widespread in biomedical science. The polyethylene glycol (PEG) nanocomposite containing MoS_2 nanosheets has been used as a multi-functional drug carrier for combined cancer therapy [78]. Also, PEG nanocomposites containing WS_2 have been used as a multifunctional agent for dual-modal CT/photoacoustic imaging in photo-thermal therapy [79]. Also, MoS_2-based nanocomposites are used in DNA sensors to detect DNA molecules [80].

Another application of GLNs nanocomposites are the increasing the impermeability of nanocomposites against oxygen that used in the food packaging industry. Most polymers used in this industry suffer from the problem of oxygen penetration. 2D nanosheets form a strong barrier against oxygen penetration due to their layered structure. For example, the nanocomposites based on cellulose nanofibers containing BNNSs prevent the penetration of oxygen. In addition, GLNs improve the mechanical properties of the nanocomposite and does not alter the brittleness [81].

6. Future outlook

The fillers based on GL nanomaterials are at the beginning of their path to expand. However, there are several fundamental challenges that must be considered before fully understanding their effects in polymer composites.

1. Distribution of fillers in the polymeric matrix is important to achieve the properties of nanocomposites. However, most of the composite processing methods are not economically optimal. Solvent processing, LBL assembly and electrospinning have a better result in dispersion of the filler but are not economically affordable. The melt processing method is economical, but the filler has no proper dispersion and the final properties are less than optimal.

2. GL nanomaterials can act as nucleating sites and affect the polymer's crystallinity. Therefore, the degree of dependence of the crystallinity value on the mechanical properties of the composites should be investigated.

3. The development and quality of nanocomposites containing GL nanomaterials depend on several factors, including the type of filler, the number of layers, the purity of the filler, the amount of dispersion in the polymer, and the interaction between the filler and the polymer matrix. However, so far, no systematic study has been done to compare the effect of aspect ratio, filler purity, functionalization degree, and the types of functional groups on the properties of nanocomposites.

7. Conclusions

Graphene-like nanomaterials and polymer-based nanocomposites demonstrate the increasing growth in technology and applications. In this study, recent advances in the production of polymer-filled nanocomposites with GLNs were investigated, properties and applications of these materials. Although these materials are in the early stages of development, their value added and their ability to address them is quite evident. Of course, one should take into account the unfulfilled expectations of graphene nanocomposites and consider the challenges and problems involved in the development of these materials that need to be solved and used them to develop polymer-filled with GLNs.

The first challenge is the production of GLNs. On the other hand, high-quality and large-scale of GLNs preparation at affordable cost is still not possible. Although recent steps have been taken for this purpose seriously, but new synthesis methods should be created to reduce the use of acid and solvent.

The second major challenge is the nanocomposite production process. The full utilization of GLNs-filled nanocomposites with the good dispersion of GLNs increases the cost-effectiveness of final nanocomposite production. Many efforts have been made to improve and enhance the properties of nanocomposites by modifying the interfacial interaction of filler and polymer matrix through functionalization or use the compatibilizers. Several studies use the functionalization of filler in order to create strong interaction between GLNs with a polymer matrix. This improves bonding between GLNs and polymer, which improves stress transfer, increases thermal stability and other properties. Efforts in this field can lead to the production of nanocomposites that have widespread use in the field of bio-detecting, drug delivery, food packaging, thermal shields, contamination absorption, electronics device etc.

Conflict of interest

The authors declare that they have no conflict of interest.

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