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# Hybrid Graphene Nanocomposites: Thermal Interface Materials and Functional Energy Materials

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## Abstract

Most existing materials may not satisfy all the fundamental requirements of modern civilization. This chapter summarizes the latest advances in the study of hybrid graphene nanocomposites and their application as thermal interface materials and some functional energy materials, in particular, for thermal management of energy and electronic devices. The main properties of hybrid graphene nanocomposites are described. The main attention is paid to the thermal properties of such materials, in particular, thermal conductivity and the possibilities of its growth due to various changes in the morphology and other properties of nanocomposites. The technology of obtaining a new nanocomposite based on mesoscopic microspheres, polymers, and graphene flakes is considered.

**Keywords:** nanocomposite, graphene, graphene nanoflake, thermal interface materials, thermal conductivity, thermal management

## 1. Introduction

The development of modern and promising materials is associated both with the need to study their fundamental properties and with their use in industrial applications, biology, medicine, and ecology [1–11]. Many of the existing materials may not satisfy all the fundamental requirements of modern civilization. This understanding prompted researchers to develop hybrid materials that may exhibit superior properties to those of the individual components. A special role in the development of new materials today is played by composites and hybrid composites. If in the base material (matrix) there are inclusions (fillers) of a certain size (microscopic, mesoscopic, or nanoscale), then the composite is classified as microcomposites, mesocomposites or nanocomposites [4, 8, 12–14]. Hybrid nanocomposites are composites in which, in addition to the base material (matrix) and nanofiller, other components of various sizes (microscopic, mesoscopic, or nanoscale) can be present. Hybrid graphene nanocomposites are composites that necessarily include carbon nanocomponents, for example, graphene in various modifications (nanoplates, nanoflakes, etc.). Hybrid graphene nanocomposites have attracted much attention recently because of their unique structure and remarkable mechanical, electrical, and thermal properties [15–20]. Recently, the development of hybrid

nanocomposites has been growing at a rapid pace due to the numerous needs in energy and electronics, construction, aviation and space technology, biology and medicine.

Currently, there are various types of hybrid composites and nanocomposites, a description of the technology and properties of which are available in the scientific literature [9, 17, 21–31]. At the same time, the class of composites associated with nanocarbon components, namely graphene and its derivatives, has the most interesting and important properties. This does not mean that other classes of hybrid composites are less important, but there are hybrid graphene composites that demonstrate the most unexpected properties and prospects of use today.

For various applications, functional energetic materials must possess not only the necessary internal parameters, but also have a special functional surface (wettability, surface physical and chemical activity, etc.). The important areas of using functional energy materials based on graphene hybrid composites may include the following: superhydrophobic surfaces for anticorrosive protection of materials, surfaces for anti-icing, and self-cleaning surfaces [21]. Such materials are also used in boiling and condensation processes. The surface wettability plays a key role in boiling heat transfer, where the heat transfer coefficient is enhanced due to the rapid departure of nucleation bubbles from the surface with a small superheat. Condensation is a common process in industry, such as in the production of electricity, heat exchangers, and so on. If the surface energy of functional materials is high enough, film condensation actively occurs on it. Such materials include metals on which a decrease in the heat transfer coefficient is usually observed due to the presence of a liquid film that has low thermal conductivity. Coating a metal surface with a superhydrophobic material leads to dropwise condensation, which allows drops of liquid to easily break off the surface and be carried away into the external stream. It is the same properties that many graphene and hybrid nanocomposites have. Boiling heat transfer is often used in heat transfer devices, such as a heat exchanger, boiler, for cooling electronic and optoelectronic devices, solar thermal and photovoltaic energy, etc. due to its high heat transfer efficiency. As shown by numerous studies, the heat transfer efficiency on a superhydrophobic surface is much higher than on a smooth surface [18, 21]. The study of graphene nanocomposites as superhydrophobic materials for applications in power engineering, electronics cooling, and other applications is still insufficient. There are several publications devoted to this problem [20, 27]. However, practical data are not available for graphene nanocomposites. Therefore, it is necessary to study the heat transfer during boiling in various modes (nucleate and bubble growth, transition, and film), as well as critical heat fluxes on superhydrophobic surfaces of graphene nanocomposites. The topic of studying graphene nanocomposites as heat transfer, evaporation, boiling, and condensation surfaces is an important and relative new direction, which should be given great attention in the future [20–27].

## **2. Graphene nanocomposites (GNC): general properties**

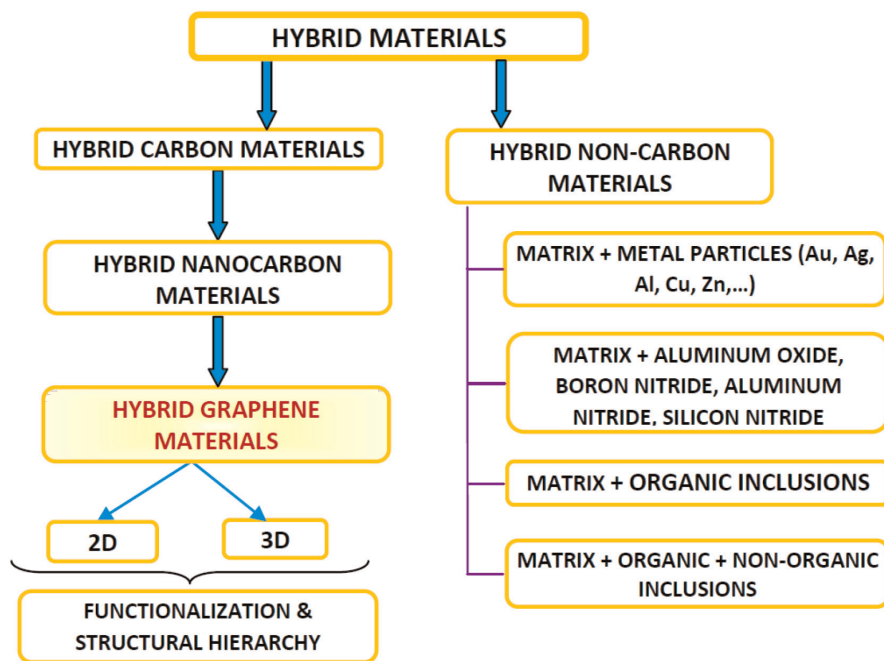
The hybrid material scheme is shown in **Figure 1**, which also shows the class of hybrid graphene composites, which will be described below. Published reviews and scientific articles contain very detailed information on the results of studies of such composites in recent years [14–18]. In **Figure 1**, the region of hybrid graphene nanocomposites (HGNC) is highlighted.

This chapter is devoted to this area of composites research. The term “graphene-related materials” is used to refer to graphene-related materials that have different names in scientific literature [1, 3–5, 8]. These include graphene oxides (GO),

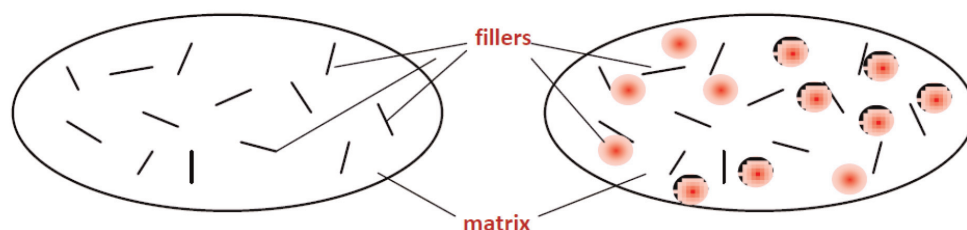
reduced graphene oxides (rGO), graphene foam (GF), graphene nanoribbons (GNR), graphene nanoplates (GNP), graphene sheets (GS), graphene nanoflakes (GNF), graphene film (Gfi), etc. The term “graphene composites” means that graphene components are placed in an organic or inorganic matrix. Moreover, the morphology of graphene components, their number, volume fraction, etc. can be completely different [24–27].

**Figure 2** gives a simple idea of standard and hybrid composites. Here, you can see that usually standard composites consist of a base (mother) matrix and one type of filler. In hybrid nanocomposites, not only more than one filler, but in most situations there should be special morphology and architecture.

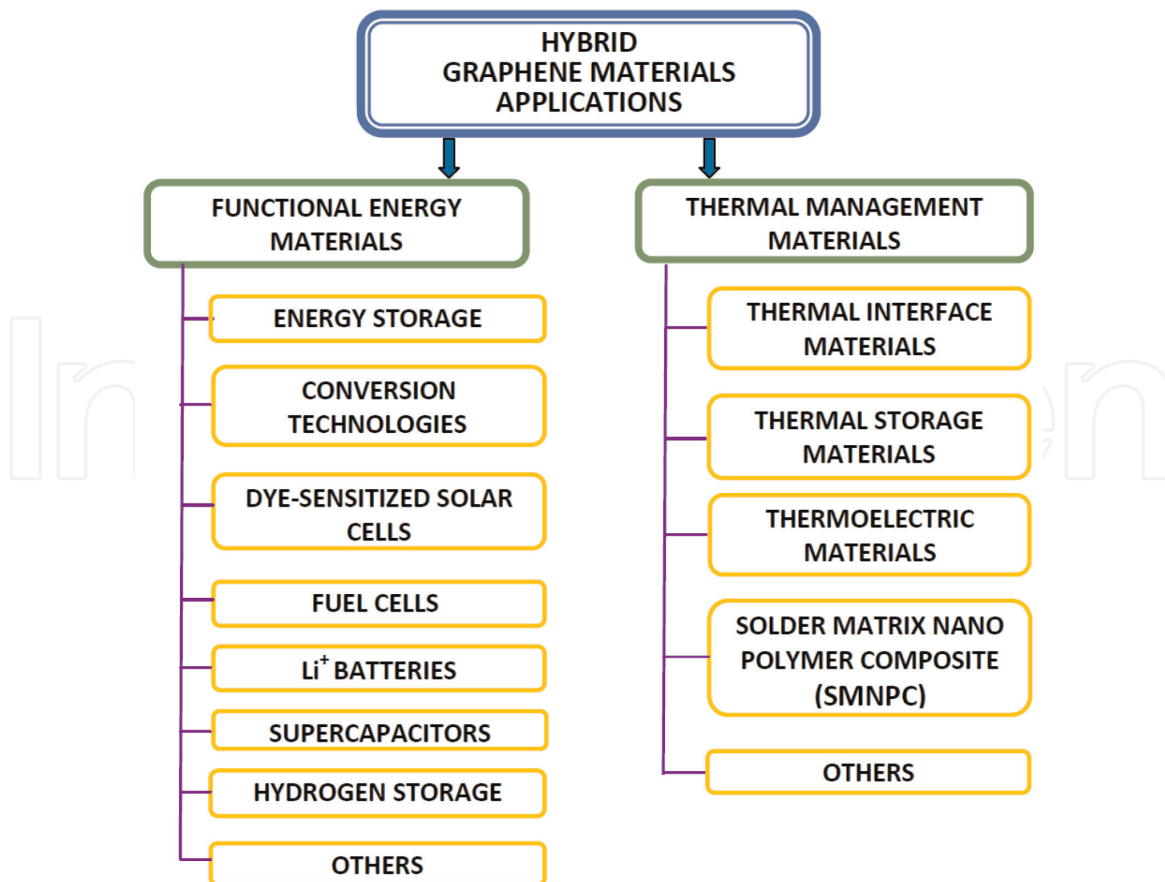
Hybrid graphene nanocomposites are currently used in various applications, as shown in **Figure 3**. Among these applications are functional energy materials for energy conservation, lithium-ion batteries, supercapacitors, fuel cells, hydrogen storage, systems for conversion solar radiation into steam and systems for producing clean and desalted water during solar heating, as well as many others [6, 18, 20–23]. Technologies and synthesis of graphene components, including graphene plates and flakes, are given in [15, 17, 19]. Currently, there are several methods for producing such graphene components on an industrial scale [19].



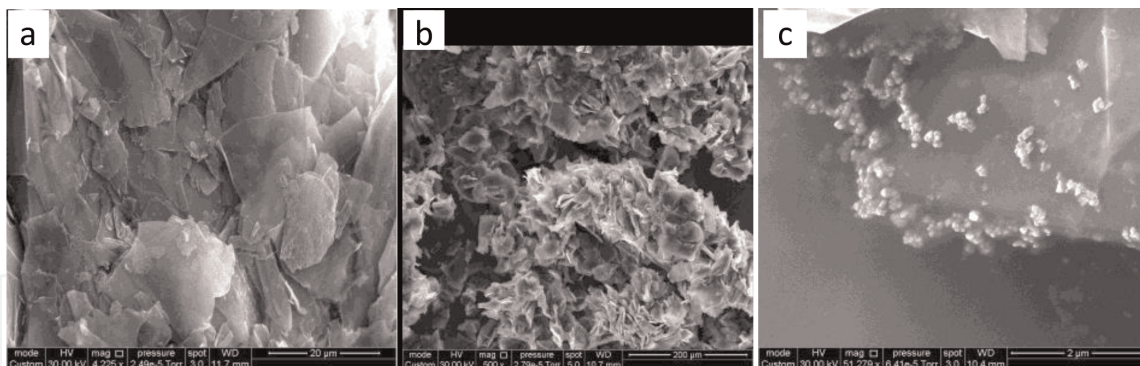
**Figure 1.**  
*Scheme hybrid graphene materials.*



**Figure 2.**  
*Conventional (left) and hybrid (right) composites.*



**Figure 3.** Scheme for hybrid graphene materials application.



**Figure 4.** Electron microscopy of hybrid graphene composites: a - graphene flakes, b - graphene flakes on polymer droplets, c - gold nanoparticles on the surface of graphene flakes.

Graphene hybrid materials have been fabricated by the cross-linking of graphene or graphene oxide (GO) through various kinds of inorganic or organic species, i.e., inorganic nanoparticles, polymers, multifunctional organic molecules, and metal ions/complexes [4, 7, 8]. More recently, a review has been published that provides many important data on graphene and hybrid nanocomposites [32]. The table contains the main research results in recent years on graphene nanocomposites [20, 28, 33–52].

As an example, **Figure 4** shows the main components when creating graphene hybrid nanocomposites. Graphene flakes with lateral (longitudinal) sizes of 10–30  $\mu\text{m}$ , a thickness of 3–5 nm, obtained by liquid-phase exfoliation of graphite in pure water (**Figure 4a**); graphene flakes on polymer droplets (prior to compression and thermal treatment and obtaining a polymer matrix (**Figure 4b**)). Gold



nanoparticles of 4–6 nm in size on the surface of graphene flakes produce hybrid graphene nanocomposites (**Figure 4c**).

The graphene-based inorganic or organic hybrid materials have been extensively investigated in various applications: as thermal interface materials, functional energy materials, energy storage, and/or conversion-related fields [32, 33]. In particular, the following were investigated:

- effect of filler loading level,
- fillers of various dimensions: one-dimensional fillers (1D fillers with high-aspect-ratio), platelet-like fillers, spherical and quasispherical fillers,
- surface treatment,
- filler orientation,
- filler agglomerates,
- formation of continuous filler network (thermal percolation effect),
- double percolation (thermal conductivity and electrical conductivity percolation effects),
- functionalization of fillers, and
- size effects.

Fillers	Category	Thermal conductivities W/(m K)
Aluminum (Al)	Metal	234
Copper (Cu)	Metal	386
Gold (Au)	Metal	315
Silver (Ag)	Metal	427
Carbon nanotube (CNT)	Carbon based	1000–4000
Carbon fiber	Carbon based	300–1000
Graphite	Carbon based	100–400
Graphene	Carbon based	2000–6000
Diamond	Carbon based	9000
$\beta$ -Silicon nitride ( $\beta$ -Si <sub>3</sub> N <sub>4</sub> )	Ceramics	103–200
Hexagonal boron nitride (h-BN)	Ceramics	185–300
Aluminum nitride (AlN)	Ceramics	100–300
Diamond like	Ceramics	1000
$\beta$ -Silicon carbide ( $\beta$ -SiC)	Ceramics	120
$\alpha$ -Alumina ( $\alpha$ -Al <sub>2</sub> O <sub>3</sub> )	Ceramics	30
Beryllium oxide (BeO)	Ceramics	270
ZnO	Ceramics	21
SiO <sub>2</sub>	Ceramics	1

**Table 1.**  
 Thermal conductivities of common types of fillers.

Filler # 1	Filler # 2	Filler # 3
h-BN	Different sized h-BN	—
h-BN	Carbon fiber	—
h-BN	Carbon nanotubes (CNTs)	—
Carbon nanotube (CNT)	Carbon based	—
Hollow glass microspheres	Nitride nanoparticles	—
Aluminum nitride (AlN)	Carbon nanotubes (CNTs)	—
SiC (nanosized)	Carbon nanotubes (CNTs)	—
Graphite	Carbon fiber	—
Graphene	BN	—
Laminated h-BN	SiC microparticles	—
Graphite nanoplatelets	Ceramics	—
Graphene nanoflakes	Metallic microspheres	—
Graphene nanoflakes	Metallic microspheres	Au, Ag, SiO <sub>2</sub> nanoparticles
Graphene nanoflakes	Carbon nanotubes (CNTs)	Metallic microspheres
Graphene nanoflakes	Graphite	—

**Table 2.**  
*Effects of hybrid fillers.*

**Table 1** presents the main fillers of polymer composites when the composites contain only one type of filler [33].

**Table 2** shows the hybrid nanocomposites options in which there are several types of fillers [33].

### 3. Thermal conductivity of hybrid nanocomposites and graphene nanocomposites

The morphology of graphene in a polymer matrix significantly affects the thermal conductivity of composites [33]. It is usually customary to separate morphology into two types: random dispersion of graphene in a polymer matrix and regular [20, 32]. Random dispersion refers to the addition of graphene to a matrix, which is performed by a simple method, such as agitation, sonication, and blending. In addition, there is usually no special method used to control the orientation of graphene in the matrix. The second type of morphology is graphene with a specific orientation in the polymer matrix (regular structure). This refers to unusual graphene structures in a polymer matrix, including orientation, three-dimensional structure (3D) and separate structure, etc. Graphene with a random orientation in the polymer matrix can be manufactured by many methods, such as solution mixing, melt mixing, and in situ polymerization, etc. [32].

Some thermal properties of graphene composites with random orientation are given in **Table 3** [20, 32, 33, 40, 42]. The special orientation of graphene can significantly affect the properties of graphene nanocomposites. In the case of hybrid nanocomposites, the situation can be even more complicated: the mutual orientation of several types of fillers can affect the final properties of graphene materials.

The specific orientations of graphene give composites special properties. The thermal properties of recent studies of graphene-polymer composites are shown in

Nanocomposites	Filler loading	Thermal conductivities W/(m K)	Thermal conductivities enhancement per wt%
Epoxy + GNS-Py-PGMA	3.8 wt%	1.91	225%
Epoxy + f-Gfs	10 wt%	1.53	66.5%
Epoxy + GNP + C750	5 wt%	0.45	23.8%
Epoxy + DGEBA + f-GO	4.6 wt%	0.72	52.3%
PVDF + GS + Al <sub>2</sub> O <sub>3</sub>	40 wt%	0.586	4.8%
Epoxy + GNP + Al <sub>2</sub> O <sub>3</sub>	12 wt%	1.49	56.4%
PBT + GNP	20 wt%	1.98	61%
PPS + GNP	37.8 vol%	4.14	49%
PI + SiCNW-GS	7 wt%	0.58	21%
SR + GNP	0.72 wt%	0.3	69.4%
PA6 + Gr-GO	10 wt%	2.14	56.9%
Epoxy + GNP	25 vol%	2.67	49.4%
PVDF + FGS + ND	45 wt%	0.66	3.9%
Epoxy + ApPOSS-Gr	0.5 wt%	0.35	115.8%
PU + IL-Gr	0.61 wt%	0.3	55.9%
PA + TCA-rGO	5 wt%	5.1	357.8%
BE + Gr	2.5 wt%	0.54	73.7%
Silicone + GNP	16 wt%	2.6	49.7%

**Table 3.**  
 Graphene composites with random orientation.

**Table 4** [32, 33, 40]. Most studies have shown that an increase in the volume concentration of the nanocomponent practically does not affect the crystal structure of materials.

Traditional polymer composites cannot meet the requirement of achieving higher thermal conductivity at relatively low filler loading. Regular orientation of fillers is important in the thermal conductivity of nanocomposites. In particular, when controlling the orientation of silicon carbide nanowires (with a very low filler loading of about 5 wt%) in epoxy resins, the thermal conductivity of the composite in the plane reached 10.1 W/m K. On the other hand, with random orientation of SiCNW nanowires in epoxy resin, the thermal conductivity was only 1.78 W/m K, and for an epoxide/silicon carbide composite in the form of nanoparticles, it was 0.30 W/m K [53]. Theoretical models of the thermal conductivity of such composites show that the correct orientation and high aspect ratio for nanowires contribute to the formation of heat transfer networks in composites, leading to the effect of thermal percolation.

Currently, the main types of thermal interface materials used have a matrix of organic compounds, for example polymers, which are filled with inorganic particles of high concentration, such as ceramic or metal. Recently, graphene nanoplates (GNPs) or nanoflakes (GNFs) [27], usually having several graphene layers, have been actively used as fillers. Due to the special morphology of the layers, as well as



Nanocomposites	Filler loading (Gr wt%)	Thermal conductivities W/(m K)	Thermal conductivities enhancement per wt%
PDMS + vertically aligned Gr film	92.3 wt%	614.85	3329%
Epoxy + multilayer Gr	11.8 wt%	33.54	1413%
Epoxy + nanofibrillated cellulose	1 wt%	12.6	910%
PVDF + large-area rGO	27.2 wt%	19.5	324%
Oriented GNF + PVDF	36.8 wt%	10	113%
Epoxy + GNS-Fe <sub>3</sub> O <sub>4</sub>	1.74 wt%	0.6	80%
Polyethylene + GNP	10 wt%	1.84	45.7%
Polypropylene+ GNP	10 vol%	1.53	59.5%
PVA+ GNP	10 wt%	1.43	58%
PVDF + GNP	10 wt%	1.47	67.3%
Epoxy + Gr + SWCNT	7.5% wt%	1.75	—
Epoxy + Gr + MWCNT	20 wt%	6.31	—
Epoxy + Ag flakes + CNT (functionalized)	35.5 wt%	160	—
Epoxy + hBN + SiCNW	95 wt%	21.7	—
Epoxy + hBNNT	30 wt%	2.77	—
PVDF + AgNW	25 vol%	1.61	1050%
Epoxy + CoNW	0.12 vol%	2.59	700
PVDF + Cu <sub>2</sub> ONW	30 wt%	0.32	170
Epoxy + SiO <sub>2</sub> (coated AgNW)	4 vol%	1.03	415
Epoxy + SiNNW	60 wt%	9.2	4281
Epoxy + BNNT	30 wt%	2.77	1360

**Table 4.**  
*Thermal properties of graphene-polymer composites.*

hybridization of the chemical bonds of the carbon lattice, such plates or flakes have a very high thermal conductivity [54, 55], which makes it possible to control the thermal conductivity of organic matrices even at very low concentrations. It was noted that an increase in the lateral size of graphene nanoflakes and the number of layers leads to an increase in their thermal conductivity, and, consequently, to the thermal conductivity of the nanocomposite. Apparently, there are an optimal number of graphene layers, which ensures low phonon scattering and leads to high thermal conductivity of nanoflakes with a small number of layers (less than 10) [56, 57].

The production of nanofilled GNP resins is crucial for the final properties of these materials, since they are highly influenced by dispersion, stratification and orientation levels, as well as the final morphology (size, waviness, imperfection) of GNP. For the creation of heat-conducting materials, dispersion, orientation, and the degree of delamination are important [58]; the presence of defects can reduce thermal conductivity; poor interaction between the matrix and nanofillers can lead to a decrease in mechanical strength and deterioration of thermal properties, etc.

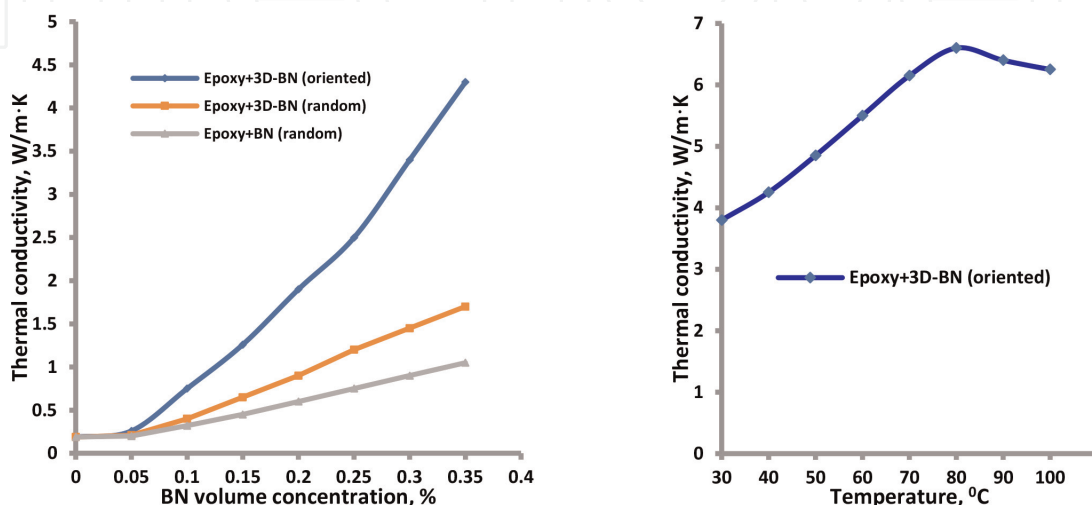
Thus, the most important task is a thorough analysis and selection of the production route and initial characteristics of GNP (functionalization and morphology) [59].

Oriented 3D-BN network composites in epoxy were made by combining self-assembly and infiltration technology using ice patterns [60]. It was shown that the resulting composites have good thermal conductivity – 4.42 W/m K and a lower coefficient of thermal expansion. The authors attribute the improvement in thermal conductivity to the following factors: well-aligned BN plates in the direction of higher thermal conductivity, since the latter is anisotropic, as well as a decrease in the boundary thermal resistance. In addition to this, apparently, there is a three-dimensional network of BN plates in epoxy resin. In particular, there is a difference in the thermal interface resistance of oriented and random composites ( $4.0 \times 10^{-7}$  and  $5.6 \times 10^{-7} \text{ m}^2 \text{ K/W}$ , respectively). Thus, the importance of orientation on the behavior of the thermal conductivity of nanocomposites is obvious. The dependence of the thermal conductivity of the nanocomposite on random and oriented plates and on their volume concentration is shown in **Figure 5** (left). **Figure 5** (right) shows the temperature dependence of the thermal conductivity of such nanocomposites. It should be noted that at a certain temperature, a drop in heat conduction is observed, which is an important factor when using such materials for thermal management.

As previously established, one of the most important factors associated with the thermal conductivity of nanocomposites filled with graphene nanoparticles (GNP) is the size of the GNP, that is, their lateral size and thickness. A relationship was established between the thermal conductivity of polymer composites and the size of GNP fillers in polymer composites.

An increase in the thickness of graphene plates and their transverse size leads to a decrease in the boundary thermal resistance between them and the matrix. In particular, for a volume fraction of GNP, 20 wt% volumetric and in-plane thermal conductivity was 1.8 and 7.3 W/m K, respectively (thermal conductivity polymer matrix 0.24 W/m K) [60].

The use of inorganic matrices is proposed in [61]. Hybrid paper with graphene/SiC (graphene hybrid paper, GHP) was developed by an easy and easily scalable filtration method followed by rapid heat treatment to grow SiC nanorods in situ between graphene sheets based on the carbothermic reduction reaction. GHP demonstrates a characteristic structure consisting of a hierarchical architecture of graphene/SiC nanorods, which leads to an increase in thermal conductivity in the plane (10.9 W/m K) by 60% compared to graphene paper. It is interesting to note



**Figure 5.**  
Thermal conductivity BN nanocomposites [60].

that graphene-based paper, if used as TIM, significantly reduces thermal conductivity through the plane when compressive force is applied. The presence of the C—Si covalent bond leads to an increase in thermal conductivity to 17.6 W/m K in the presence of compressive force. Eliminating the aging problem of conventional polymer-based TIMs, GHP with its characteristic inorganic structure has great potential for use as highly effective TIMs with good thermal and chemical stability.

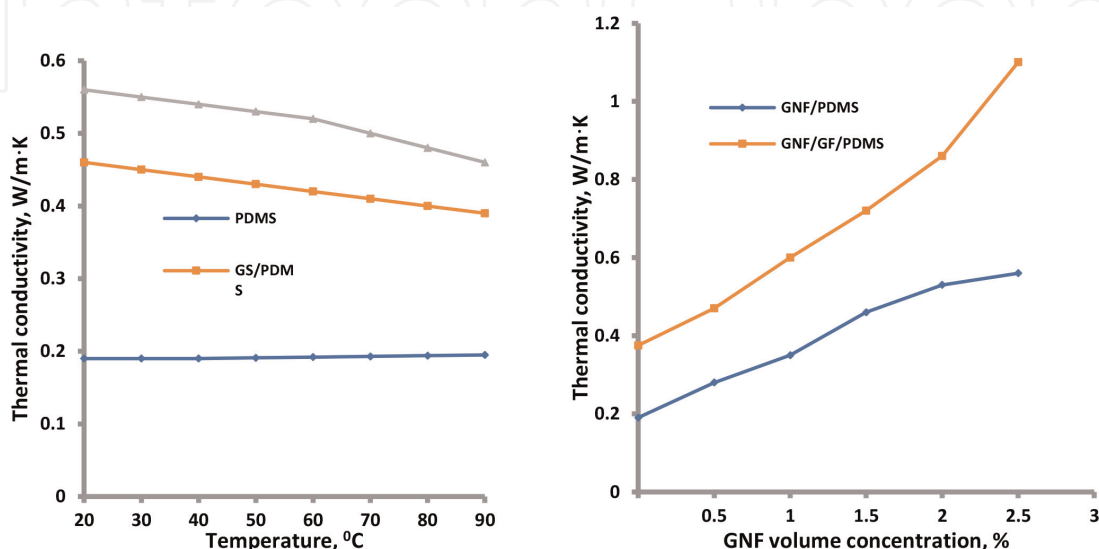
Three modern TIMs based on graphene are compared, including dispersed graphene/polymers, graphene framework/polymers, and inorganic monoliths based on graphene [28, 62]. Their advantages and limitations are discussed in terms of application. In addition, potential strategies and future research directions in the field of the development of highly efficient graphene-based TIMs are discussed.

Recently, a unique design of hybrid nanocomposites was used: microscale flakes Ag and multiwalled carbon nanotubes (MWNTs), which were decorated with Ag nanoparticles (nAgMWNT), were placed in a polymer matrix [63]. It was shown that even a small volume fraction of nAgMWNT (2.3 vol%) in epoxy matrix leads to the creation of effective phonons transfer paths between Ag flakes (35.8 vol%) (thermal conductivity  $\sim 160$  W/m K). The successful dissipation of computer CPU heat using nAgMWNT-Ag-flake-epoxy TIM demonstrates the superior ability to cool electronics.

In addition to graphene hybrid nanocomposites based on epoxy resin, other polymers are also used. In particular, polymer composites consisting of graphene foam (GF), graphene sheets (GSs), and flexible polydimethylsiloxane (PDMS) were made, and their thermal properties were studied [46]. Due to the unique interconnected GF structure, the thermal conductivity of the GF/PDMS composite reaches 0.56 W/m K, which is approximately 300% higher than that of pure PDMS and 20% higher than that of GS/PDMS composite with the same graphene load of 0.7 wt%. **Figure 6** shows the dependence of thermal conductivity on temperature and volume fraction.

Coefficient of thermal expansion is  $(80\text{--}137) \times 10^{-6}/\text{K}$  in the range of 25–150°C, which is significantly lower than that of composites GS/PDMS and pure PDMS.

In addition, it also exhibits excellent thermal and dimensional stability. Later, these authors added a different amount of multilayer graphene flakes (MGF) to the composition of 0.2 vol.% GF/polydimethylsiloxane (PDMS). It was noted that in such a graphene hybrid nanocomposite, a synergistic effect between MGF and GF was achieved in improving the thermal conductivity of polymer composites. When



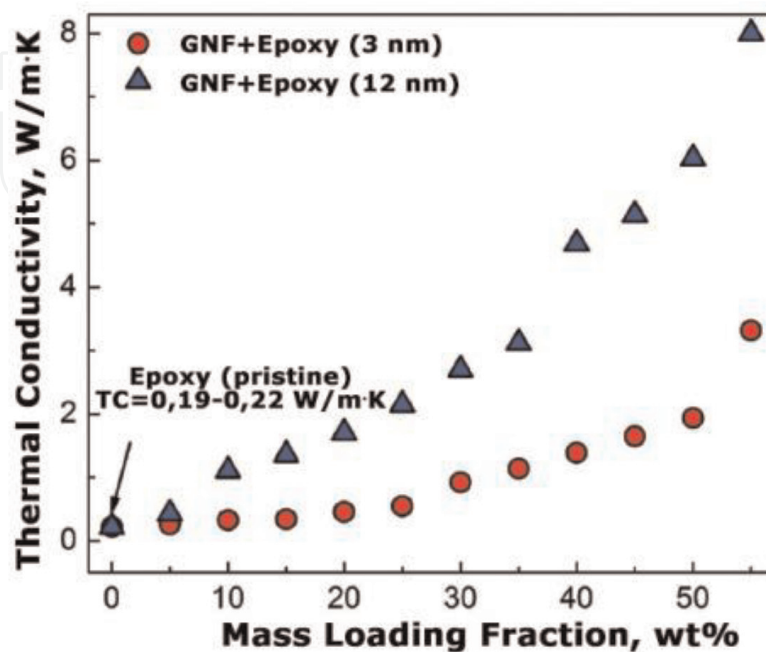
**Figure 6.** Thermal conductivity on temperature (left) and volume fraction GNF (right).

the MGF content is 2.7 vol%, the thermal conductivity of the MGF/GF/PDMS composite reaches 1.08 W/m K, which is 80, 184 and 440% higher than that of the MGF/PDMS composites 2.7 vol%, GF/PDMS and pure PDMS, respectively. The MGF/GF/PDMS composite also exhibits excellent heat resistance. Adding MGF and GF slightly reduces elongation at break, but significantly increases Young's modulus and tensile strength of composites compared to pure PDMS. The good performance of the MGF/GF/PDMS composite makes it a good TIM for possible applications in thermal control of electronics.

An important area of the use of graphene nanocomposites is functional energy materials, among which a special role is played by phase change materials (PCM) for thermal energy storage (TES) used in a wide range of applications, including control of thermal electronic devices and thermal storage of solar energy. It is proved that this is an effective method for thermal power plants due to its high heat capacity and small temperature changes [41]. However, most PCMs have low thermal conductivity, which reduces the efficiency of the thermal storage device. In order to increase the PCM heat transfer ability and prevent the leakage of molten PCM, the TES system requires a heat exchange amplifier and a container [2–8]. Researchers used metal foam, additives, or fins to increase PCM thermal conductivity. However, these amplifiers add significant weight to the TES, and some of them are incompatible with PCM. This is the reason for the search for hybrid nanocomposites with a wide range of properties. First of all, in recent years, attention has been paid to hybrid graphene materials [21–23].

The new three-dimensional hierarchical graphene foam material (HGF) was obtained by filling the pores of GF with hollow networks of graphenes [38]. A hybrid nanocomposite based on paraffin (PW, matrix) and HGF showed a thermal conductivity of 744% higher than that of pure PW. To improve the properties of such materials, further hybrid graphene materials with the addition of multiscale fillers will undoubtedly be needed in the future [64].

It was found that the increase in thermal conductivity of composites with thicker graphene fillers (GNF) from several layers is greater than that of composites with thinner fillers with the same loading fraction [48] (**Figure 7**). The deviation found from the linear dependence of thermal conductivity on the volume concentration of



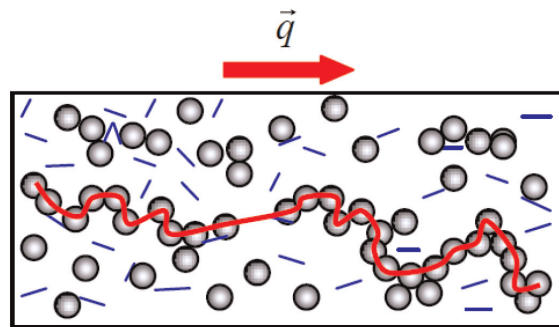
**Figure 7.**  
Thermal conductivity on loading fraction and thickness GNF [48].



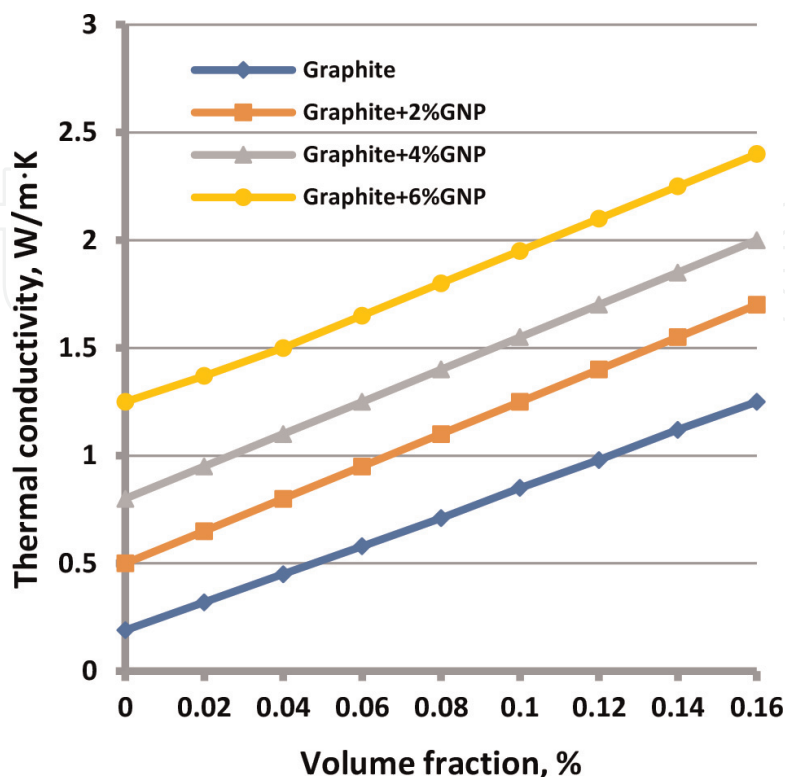
graphene nanoflakes indicates the beginning of thermal percolation in graphene composites.

The increase in thermal conductivity of hybrid nanocomposites can be achieved in various ways: the use of fillers with high thermal conductivity, the use of hybrid fillers, the creation of a new architecture of nanocomposites, including the effects of thermal percolation, etc. In particular, the last effect can be demonstrated: the heat flow through the effect of thermal percolation is shown in **Figure 8**.

In [65], a new tunable HGNC containing a combination of two different fillers based on carbon, graphene nanoplates (GNP) and graphite was proposed. By adjusting the concentration ratio of GNP: graphite and the total concentration of fillers, the authors were able to fine-tune the thermal conductivity and workability of HGNC. The following filler parameters were used: the average length of the filler particles was determined by measuring 100 particles for each filler material and the sizes of the different fillers, when imbedded in the epoxy matrix, are  $19 \pm 3$  and  $27 \pm 4 \mu\text{m}$  for the GNP and the graphite, respectively. **Figure 9** shows the dependences of the thermal conductivity of nanocomposites on the volume fraction of graphite. It is clearly seen that such dependencies are linear. With an increase in the



**Figure 8.**  
Heat flow through the effect of thermal percolation.



**Figure 9.**  
Thermal conductivity of hybrid composites ( $T = 25^\circ\text{C}$ ) as a function of the graphite volume fraction [65].



volume fraction of graphene nanoplates, the overall thermal conductivity increases, which corresponds to the general trend of the effect of graphene nanoplates on heat transfer.

To optimize the design of composite materials, the authors also studied the effect of viscosity of the starting material and built a phase diagram of the concentration-thermal-conductivity viscosity. Thus, this ensures not only the selection of the thermal conductivity of the desired nanocomposite, for example, for TIM, but also the manufacturability of the material itself.

## 4. New hybrid graphene nanocomposites

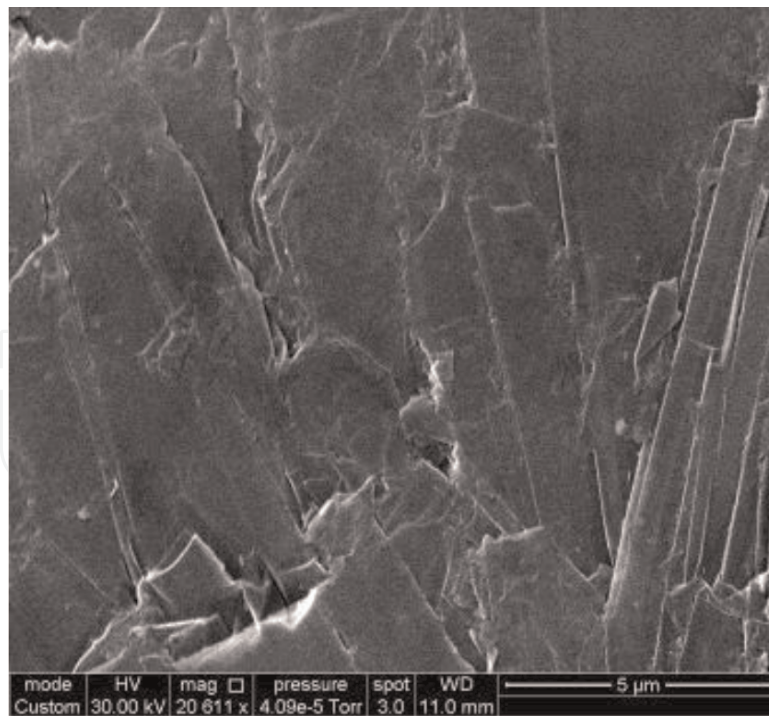
### 4.1 Hybrid graphene nanocomposites: preparation and properties

When creating hybrid graphene nanocomposites, fillers of approximately the same size, for example, nanoscale, are usually used. Several studies have attempted to introduce microsized components along with nanoscale components. However, for some reason, it was not possible to achieve a noticeable increase in the thermal conductivity of such composites [66–69]. In the framework of this study, an attempt was made to combine the remarkable properties of graphene flakes with metal microparticles, which in themselves have high thermal conductivity. On the other hand, it was assumed that the use of equally sized (monodisperse) metal microspheres would help to make a regular controlled structure of the composite. We also note that the use of metal particles makes it difficult to use a similar material for thermal interfaces, since the latter must be nonconductive. This problem was solved by the fact that the microspheres, for example, tin, were partially oxidized on the surface, which led to a significant potential barrier to the flow of electric current (noticeable electrical boundary resistance). At the same time, as the research results showed, the boundary thermal resistance of the metal + oxide film boundary was always less than the boundary thermal resistance at the boundary of the microsphere with the polymer.

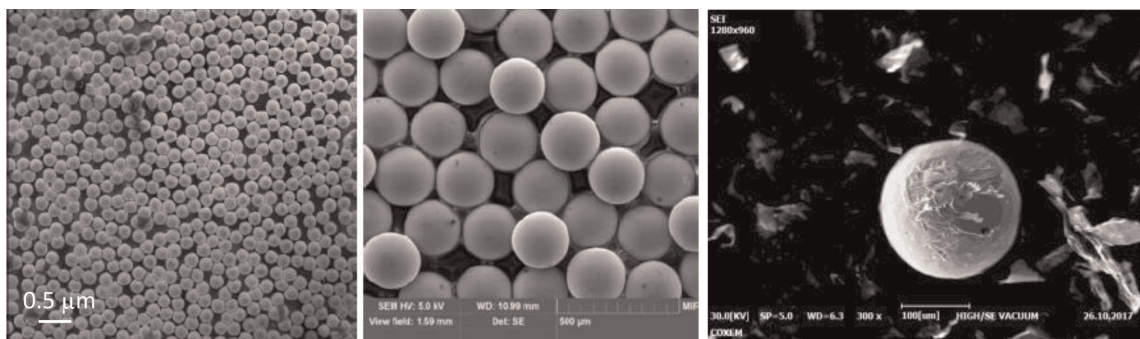
Hybrid composite functional energy materials require new approaches, the selection of new components, and their multiscale properties. New architectures have been developed for hybrid composites based on metal microspheres, polymers (e.g., epoxy), and graphene nanoflakes (GNF). According to the technology described in [66, 67], graphene nanoflakes with lateral sizes of 5–20  $\mu\text{m}$  and 3–10 layers of graphene were obtained.

Electron microscopy of graphene nanoflakes is shown in **Figure 10**. It is clearly seen that graphene flakes can be stacked (by filtration) in regular structures. After that, the microspheres (100–150  $\mu\text{m}$ ) from Sn, Pb, and Er<sub>3</sub>Ni (production of the Moscow Power Engineering Institute) were placed in a petri dish and a nanocolloid solution of graphene flakes was poured into it (**Figure 11**). **Figure 6** shows metal microspheres from Sn coated with graphene nanoflakes. It is clearly seen that the resulting structure is very regular, and nanoflakes can adhere well to the microspheres. It should be noted that epoxy resin and polyurethane interact well with graphene flakes and metal microspheres, with significant adhesion. This allows you to create dense structures you need morphology. More detailed description of materials and methods is given in our publications [66, 67]. For the created hybrid graphene nanocomposites, the mechanical, electrical, and thermal properties were investigated. Below are the results on the thermophysical characteristics of such materials.

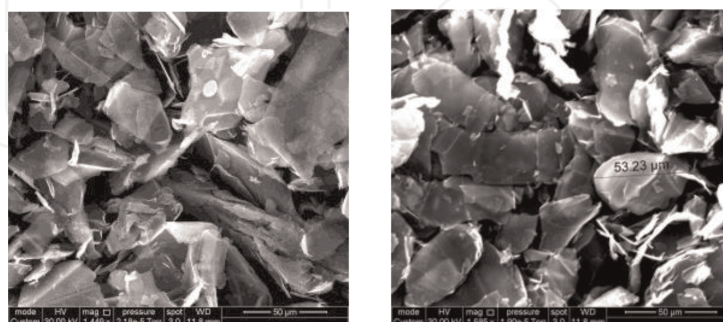
**Figure 12** shows electronic images of graphene flakes in various polymer matrices.



**Figure 10.**  
*Electron microscopy of graphene nanoflakes.*



**Figure 11.**  
*Metal microspheres from Sn coated with graphene nanoflakes.*

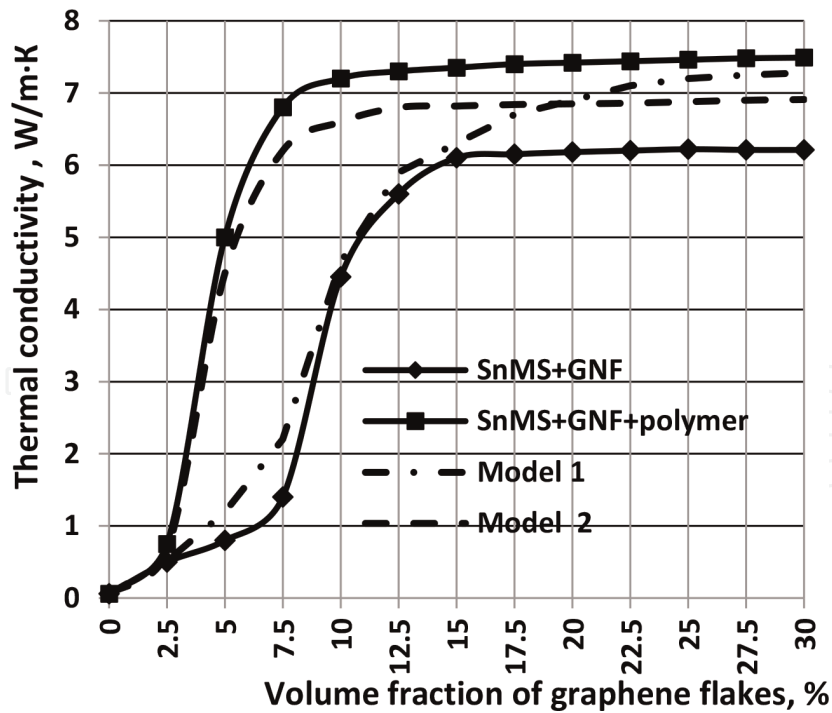


**Figure 12.**  
*The structure of graphene nanoflakes in a polymer matrix (left, polyurethane and right, epoxy resin).*

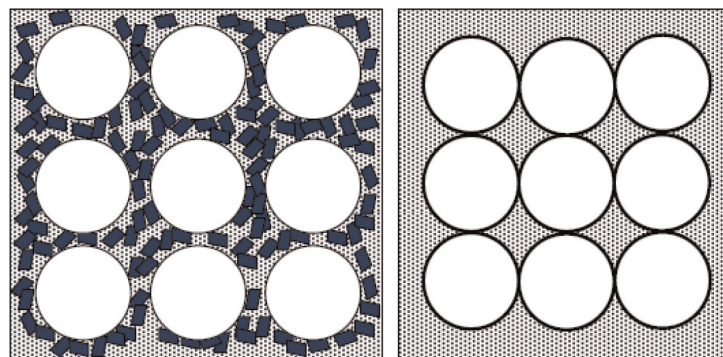
Differential calorimeter and laser flash methods were used to study the thermal conductivity of the developed composites. The results are shown in **Figure 13**.

#### 4.2 Thermal conductivity model of hybrid nanocomposites

**Figure 14** shows two types of hybrid thermal interface materials with graphene flakes (dark inclusions), metal microspheres, and a polymer (gray field). On the left



**Figure 13.**  
 Thermal conductivity as a function of volume fraction of graphene flakes.



**Figure 14.**  
 Structure HGNC model.

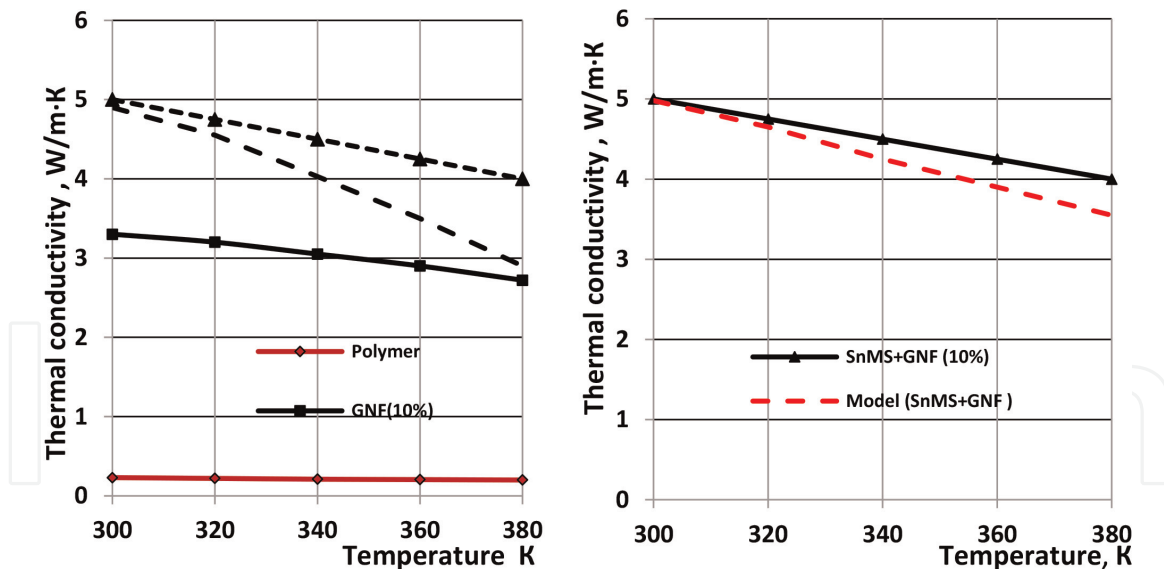
are free-packed microspheres without polymer, on the right are dense packaging of microspheres, between which graphene flakes are located, the adhesive of the nanocomposite is polymer (graphene flakes are located on the surface of the microspheres).

The thermal conductivity of hybrid nanocomposites was calculated within the framework of a modified model of the effective medium, which leads to the following expression for the effective thermal conductivity of the thermal interface

$$\lambda_{TIM} = \frac{3\lambda_m + 2\phi \left\{ \lambda_{GNF}^p \left[ 1 + (2R_K \lambda_{GNF}^p / L) \right]^{-1} - \lambda_m \right\}}{3 - \phi [1 - (2R_K \lambda_m / \delta)]} \quad (1)$$

where  $\lambda_m \approx 0.21$  W/m K is the thermal conductivity of the matrix (polymer-epoxy resin),  $\lambda_{GNF}^p$  is the thermal conductivity along the graphene flakes plane (GNF in-plane thermal conductivity), ( $\lambda_{GNF}^p \approx 1670$  W/m K),  $R_K \approx 6 \times 10^{-8}$  m<sup>2</sup> K/W is the boundary thermal resistance (Kapitsa resistance) between the polymer and GNF (estimated),  $L$  is the typical longitudinal size of graphene flakes (in our case  $L \approx 10-20$   $\mu$ m), and  $\delta \approx 3-3.5$  nm is the thickness of GNF.





**Figure 15.**  
Dependences of thermal conductivity for various composites.

The results of calculating the effective thermal conductivity by the above ratio are presented in **Figure 15**. It is clearly seen that with an increase in the volume fraction of graphene, the thermal conductivity monotonically increases. However, both for the microsphere + graphene composite and for the composite with the polymer, it saturates (for the case without polymer, approximately starting from 7.5%, for the case with polymer, from 12.5%). At the same time, it is easy to see that the model for freely mixed microspheres, GNF, and polymer leads to increasing thermal conductivity, while in the experiment, the latter is saturated. At the same time, with a GNF volume fraction of about 20%, the difference is more than 10%.

Thus, for such a system, the experiment shows a lower value of the heat transfer efficiency, which, apparently, is associated with a large value of the boundary heat resistance. For the case of the second type (dense hybrid nanocomposites), the situation is completely different. In this case, the calculation predicts a lower value of thermal conductivity at all volume concentrations of GNF. In our opinion, this fact speaks of a specific phenomenon of “thermal percolation,” the mechanism of which is discussed in more detail below.

The temperature dependences of the effective thermal conductivity of hybrid nanocomposites were also calculated (**Figures 13 and 15**). Calculations showed that thermal conductivity with temperature decreases more than in experiment, and the difference between the calculated and experimental values at a temperature of 380 K is more than 33%. This is a very strong difference in thermal conductivities, which may also indicate the influence of specific mechanisms not taken into account in theoretical models.

#### 4.3 “Thermal percolation” through the interface and modification of the ratios for effective thermal conductivity

Usually, when considering the boundary thermal resistance of Kapitza, it is assumed that the thermal interface does not change with external exposure. On this basis, two main models of the boundary thermal resistance are formulated—the models of acoustic and diffusion impedance: in the first model, it is assumed that phonons scatter elastically (specularly) at the boundary; in the second, there is diffuse scattering (phonons forget the incidence conditions at the boundary); lose memory during scattering) and the probability of passing through the interface

depends on the ratio of the densities of phonon states on each side. On the other hand, if an external action can change the interface, then one must take into account the behavior of the nonequilibrium phonon function when approaching the interface. It is generally believed that phonons are suitable for the interface in ballistic mode (without internal resistance of the interface), and all temperature drop is formed on the interface itself. We define the interface between the two materials 1 and 2; phonons that fall from body 1 and have a wave vector for the mode can either be reflected back to 1 or pass to body 2. We set the probability of passage from 1 to 2 equally, then the thermal boundary conductivity determines the heat flux from 1 to 2 for a given temperature difference in the form

$$G = \frac{1}{2(2\pi)^3} \sum_i \int_{\vec{k}} \Xi_{12}(\vec{k}, i) \left[ \hbar^2 \omega_i^2(\vec{k}) / k_B T^2 \right] \vec{v}_i(\vec{k}) \times \vec{n} \exp \left[ \hbar \omega_i(\vec{k}) / k_B T \right] \left[ \exp \left( \hbar \omega_i(\vec{k}) / k_B T \right) - 1 \right]^{-2} d\vec{k} \quad (2)$$

where  $\omega_i(\vec{k})$ ,  $\vec{v}_i(\vec{k})$  are the frequency and group velocity of phonons, respectively, with a wave vector  $\vec{k}$  for  $i$  mode in medium 1;  $\vec{n}$  is the unit normal wave vector to the surface between the bodies 1 and 2. If the dispersion relation for phonons  $\omega_i(\vec{k})$  is known, as well as the probability of propagation  $\Xi_{12}(\vec{k}, i)$ , then the integral can be calculated in explicit form. It is clear that the phonon spectrum on both sides of the boundary is known very approximately. Therefore, in the gray approximation, all quantities included in the expression (2) were calculated. Despite the low accuracy of this approximation, it was possible to calculate the basic quantities for heat transfer through the interface.

In the diffusion model, it is assumed that phonons falling from 1 to 2 forget their state and scatter with the same energy in another medium  $\Xi_{21}(\omega') = 1 - \Xi_{12}(\omega')$ . This means that the transmission coefficient is the same for similar states, i.e., passing from medium 2 to medium 1 takes place. We assume that the scattering is elastic, so that the phonon frequency does not change. In this situation, it is possible to record the probabilities of passage from medium 1 to medium 2 and vice versa in the form of transmission coefficients and. Moreover, the reflection probabilities are respectively equal. It is also believed that the probabilities of passage and reflection in the sum are equal to unity. If the temperatures on both sides of the interface are the same, then the phonon fluxes from medium 1 to 2 and vice versa are equal. If and are phonon flows incident on the interface from each side, then there is a relation  $\Xi_{12}(\omega)j_1(\omega) + \Xi_{21}(\omega)j_2(\omega) = 1$  and  $\Xi_{12}(\omega) = [1 + j_1(\omega)/j_2(\omega)]^{-1}$ . The obtained relations for the phonon transmission coefficients through the interface, taking into account the mismatch in the limiting cases of the acoustic model (AMM) and diffusion model (DMM), solve the problem of determining the thermal contact resistance in the macroscopic approximation. Bearing in mind the above relations for the boundary thermal resistance, we obtain corrections to the effective thermal conductivity, which was used earlier.

The main idea is that when a hybrid nanocomposite is compressed between metal microspheres, an extremely thin layer of polymer with GNF appears, and the concentration of the latter exceeds the threshold of “thermal percolation”; i.e., the heat flux almost passes through graphene flakes. In this case, the thermal conductivity should noticeably increase compared with the case of a nanocomposite with thick polymer interlayers. Indeed, calculations of the percolation conditions lead to the conclusion that with a GNF volume fraction inside the polymer layer exceeding



48%, a regime of direct phonon propagation along and across graphene flakes arises. In this case, an additional contribution to the heat flux appears, which is shown in **Figure 15**. It is clearly seen that compared with **Figure 13** where the difference at a temperature of 380 K was more than 33%, taking into account thermal percolation, the difference at this temperature is only 11%. This fact indicates the importance of considering the heat transfer in hybrid nanocomposites to take into account the inhomogeneous distribution of GNF inside the polymer interlayer. Thus, the analysis of heat transfer in hybrid nanocomposites consisting of graphene flakes, monodisperse metal microspheres and polymers showed a very complex behavior of heat transfer. The heat transfer mechanisms calculated on the basis of the modified theory of effective thermal conductivity showed that the main contribution to the heat flux comes from the boundary thermal resistance between microspheres, graphene flakes, and thin layers of polymers. By comparison of the obtained results with the experimental data published by us earlier, it is shown that the proposed model correctly describes the thermal conductivity of the hybrid nanocomposites; however, at high temperatures, there are very significant differences from the experimental data, which can be explained by a decrease in the boundary thermal resistance at the interface due to “thermal percolation.” In our opinion, more thorough studies of these effects are necessary in order to identify the nature of heat transfer in complex hybrid nanocomposites based on graphene flakes. Only this will allow confidently creating and calculating thermal interface materials for thermal stabilization and cooling of electronics and energy devices.

Prospects for the use of hybrid graphene nanocomposites in the future are very interesting and may bring many unexpected results.

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