



Phase Change Materials with Enhanced Thermal Conductivity and Heat Propagation in Them

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Abstract: The review contains information o; n the properties of phase-change materials (PCM) and the possibilities of their use as the basis of thermal energy storage. Special attention is given to PCMs with a phase transition temperature ranging between 20 and 80 °C since such materials can be effectively used to reduce temperature variations in residential and industrial rooms. Thus, the application of PCMs in the construction industry enables one to considerably reduce the power consumption and reduce the negative environmental impact of industrial facilities. Thermophysical characteristics of the main types of PCMs are presented. The heat balance for a room with walls made of PCM-added materials is estimated. The calculations demonstrate that such structures can stabilize the temperature in practical applications as a result of the usage of such materials. The construction of a thermal accumulator on the basis of PCM is proposed and analyzed. This facility uses water as a working fluid and paraffin as a PCM. The thermal accumulator has a modular structure so that the number of similar modules is determined by the quantity of energy to be stored. The potential of wide application of PCMs as a basis for thermal energy storage is rather limited due to a very low conductivity (less than 1 W/(m K)) inherent to these materials. This drawback can be overcome by adding carbon nanoparticles whose thermal conductivity is four to five orders of magnitude greater than that of the matrix material. The problem of fabrication of polymer composites with enhanced thermal conductivity due to nanocarbon particles doping is discussed in detail.

Keywords: phase change materials; thermal conductivity; carbon nanoparticles

1. Introduction

An intense enhancement of energy production and consumption impacts the environment negatively and requires increased expenditures. Estimations (see, for example, [1]) indicate that the global energy consumption enhances by approximately 30% in a decade. At the same time, about 40% of all energy generated in the world is consumed for heating and cooling residential and industrial buildings. In this situation, the development of new technologies permitting us to decrease or, at least, inhibit the energy consumption growth without decreasing the current living standards and the material production level, appears to be among the top priority problems facing power engineering. One of such technologies is based on the usage of phase-change materials (PCM). These materials can store or release a large amount of energy as a result of a phase transition at a change in the temperature. Building panels containing PCMs enable a considerable decrease of daily temperature variations in residential and industrial buildings without additional expenditures. Thus, the model calculations [2] imply that the utilization of panels with 20% PCM content lowers the amplitude of daily temperature variation in the constructing buildings by as much as 38%. Panels containing PCM microcapsules provide even a much greater decrease in the amplitude of daily temperature fluctuations (up to 80%) without using heat sources or air conditioning [3]. As it follows from the measurements [4], the usage of PCM-based thermal accumulating panels in the construction of residential and industrial buildings can save approximately 15% of the energy consumed for their heating and air conditioning. As a



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Copyright: © 2022 by the author. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). result, approximately 10% of all the energy generated in the world can be saved, which promotes a reduction in the negative environmental impact of the power industry.

Thermal energy accumulators on the basis of PCMs can be utilized not only in the construction industry but also in energy-storage devices of solar and wind power engineering as well as in overheating protection systems of complex electronic systems, supercomputers, or other radio-electronic hardware. The prospects for the application of PCMs in thermal and solar power engineering as the basis for energy accumulators, as well as in electronics and the instrument-making industry, stimulate active research efforts in many laboratories around the world [1–32]. The results of these and some other investigations performed in recent years were represented in many reviews and monographs [33–42].

However, the wide spread of PCM-based thermal energy accumulators is hindered by a set of problems. First of all, the very low thermal conductivity of most PCMs causes high inertia of heat accumulation. The thermal conductivity of most of PCMs accounts for about $\lambda \approx 0.2$ –0.5 W/m K, which corresponds to the typical value of the thermal diffusivity of the material $a \approx (2-5) \times 10^{-7} \text{ m}^2/\text{s}$. The time τ required for the heat propagation through a material layer of d = 0.1 m in thickness is estimated by the relation $\tau \sim d^2/a$ and accounts for several hours. For this reason, PCM-based thermal accumulators respond with a large delay to a change in the ambient temperature which makes utilization of such storage hardly workable. Therefore, the problem of the development of PCM-based materials with enhanced heat conductivity becomes the key one. One of the approaches to overcome this problem is in doping a PCM with nanocarbon particles (such as nanotubes, graphene, or soot), whose heat conductivity exceeds that PCM by 4-5 orders of magnitude [43,44]. Another approach to the usage of PCMs in the building design relates to the inclusion of a PCM into thin microcapsules for which the heat exchange time can be shortened down to a second scale by decreasing the size of capsules. This approach has been considered in detail by the authors of [29], who described different forms of PCM capsulation.

The usage of PCM in building construction and in energy storage systems requires the statement and solution of a set of tasks of both technological and theoretical character. First, one should mention the problem of preparation of a spatially homogeneous PCMbased composite material doped with carbon nanoparticles avoiding the known trend of carbon nanoparticles to the aggregation. The next task relates to the determination of the dependence of the thermal conductivity of a PCM based material on the content of doped particles having various geometry and thermophysical properties as well as the heat propagation through a non-homogeneous media depending on the gradients of the doped particle content and phase transition latent heat. All these issues have been discussed in the present article, which also contains a review of investigations addressed to determining physicochemical characteristics of PCMs and their application in thermal energy storage systems. Special attention is paid to the problem of preparing PCMs with enhanced thermal conductivity.

2. Physical, Chemical, and Thermophysical Characteristics of PCMs

We are interested in PCMs having the phase transition temperature in the range between 0 and 100 °C and the phase transition latent heat exceeding notably the product of the heat capacity by the working temperature range (several dozen degrees Celsius). The most common and readily available materials possessing these requirements are paraffin wax, fatty acids, and salt hydrates. Thermophysical characteristics of some of these materials have been presented in Tables 1–3. A diagram showing the interconnection between the phase transition temperature and enthalpy of most known phase change materials is shown in Figure 1. As is seen, all the PCM mentioned in the tables possess rather low thermal conductivity, which makes the problem of the enhancement of this parameter a very topical one.

Number of Carbon Atoms in Molecule	Phase Transition Temperature, °C	Melting Heat, J/g	Liquid State Density, kg/m ³	Thermal Conductivity, W/m K
9–12	−9 to −53	184	686	0.15
13–16	-6 to 18	196	716	0.19
16–18	18 to 28	212	734	0.21
16–28	42 to 44	214	765	0.21
20–33	48 to 50	218	769	0.21
22–45	58 to 60	221	795	0.21
24–50	66 to 68	221	830	0.21

Table 1. Thermophysical properties of commercial paraffin waxes [27] with a specific heat capacity of 2.1 J/g K.

Table 2. Thermophysical properties of fatty acids [27].

Acid	Chemical Formula	Phase Transition Temperature, °C	Melting Heat, J/g	Liquid State Density, g/cm ³	Specific Heat Capacity, J/g K	Thermal Conductivity, W/m K
Caprylic	CH ₃ (CH ₂) ₆ COOH	16	128	0.862 (80 °C)	-	0.148
Capric	CH ₃ (CH ₂) ₈ COOH	32	136	0.866 (40 °C)	-	0.149
Lauric	CH ₃ (CH ₂) ₁₀ COOH	42–44	155	0.870 (50 °C)	1.6	0.147
Myristic	CH ₃ (CH ₂) ₁₂ COOH	54	158	0.840 (80 °C)	1.6	-
Palmitic	CH ₃ (CH ₂) ₁₄ COOH	63	159	0.847 (80 °C)	-	0.165
Stearic	C ₁₇ H ₃₅ COOH	70	191	-	-	0.172

Table 3. Thermophysical properties of salt hydrates [27].

Substance	Chemical Formula	Phase Transition Temperature, °C	Melting Heat, J/g	Liquid State Density, g/cm ³	Specific Heat Capacity, J/g K	Thermal Conductivity, W/m K
Potassium phosphide hydrate	KP·4H ₂ O	18.5	231	1.455	1.83	-
Calcium chloride hydrate	CaCl·6H ₂ O	29.7	171	1.710	-	0.60
Sodium sulphate hydrate	$Na_2SO_4 \cdot 10H_2O$	32.4	254	1.485	1.93	0.54
Sodium hydrogen phosphate hydrate	$Na_2PO_4 \cdot 12H_2O$	35.2	280	1.420	1.55	0.59
Zinc nitrate hydrate	Zn(NO ₃) ₂ ·6H ₂ O	48.0	147	2.065	1.34	-
Sodium dithionite hydrate	$Na_2S_2O_4{\cdot}5H_2O$	78.0	201	1.600	1.46	-
Barium hydroxide hydrate	Ba(OH) ₂ ·8H ₂ O	116.0	267	2.180	1.17	-
Magnesium chloride hydrate	MgCl ₂ ·6H ₂ O		165	1.570	1.72	-

The most attractive materials among those shown in Figure 1 and Tables 1–3 possess the phase transition temperature in the room temperature range from 20 to 30 °C. These materials can be used in the construction of residential or industrial buildings as a basis for heat accumulators. The latent heat of phase change, *L*, of materials with a room temperature of the phase transition ranges from 100 to 200 J/g, which is approximately two orders of magnitude greater than the corresponding amount of the energy required to heat the material by 1 °C. The thermal conductivity of PCMs is $\lambda \approx 0.2-0.5$ W/(m K), which corresponds to the thermal diffusivity of $\approx (2-5) \times 10^{-7}$ m²/s.



Figure 1. Relationship between the melting enthalpy and phase transition temperature for different types of PCM [38].

The set of PCMs includes organic compounds, inorganic compounds, and eutectic mixtures. The class of organic PCMs is divided into paraffin waxes and nonparaffin compounds, which include fatty acids, esters, alcohols, glycols, etc. The advantages of organic PCMs are a wide phase transition temperature range, chemical stability, no susceptibility to corrosion, and a phase transition temperature proper for room temperature stabilization. Fatty acids, which are generally presented by the formula $CH_3(CH_2)_{2n}COOH$, are stable at cycling. The combination of different fatty acids can yield a material with a melting temperature range of 20–30 °C [38]. However, most of the organic PCMs are not stable at elevated temperatures. The main drawback of the usage of fatty acids as heat storage construction materials is their high price, which exceeds that of paraffin wax by 2.0–2.5 times.

Paraffin waxes present the main material used in thermal energy accumulators. Paraffin waxes with a melting temperature between 20 and 70 °C are used in pilot energy storage systems. These PCMs are considered usually in model calculations addressed to improve the performance of these systems. The intrinsic disadvantage restricting the practical application of thermal accumulating systems on the basis of paraffin waxes is the rather low thermal conductivity of paraffin (approximately 0.2 W/(m K)). Besides that, paraffin waxes experience a large volume change during the phase transition. The cost of paraffin waxes is rather high compared to salt hydrates.

The application of salt hydrates, as well as paraffin waxes, in heat storage materials with phase change also appears promising. The comparison of data presented in Tables 1–3 indicates that salt hydrides possess the phase transition enthalpy exceeding that of paraffin waxes by 1.5–2.0 times, while the specific heat capacity is 30–50% lower than that of fatty acids and paraffin waxes. The thermal conductivity of salt hydrides is relatively high, two to four times greater than that of other types of PCMs. Salt hydrates are not expensive and nonflammable. However, their main drawback is a rather bad compatibility with metals because an arrangement of salt close to the metal surface promotes corrosion. In addition, such compounds are hardly useful for impregnation into porous construction materials. Metallic PCMs have a quite high phase transition temperature that makes them unsuitable for construction.

Inorganic PCMs include eutectics, which present mixtures of many materials in different proportions. Eutectics can be divided into three groups according to their consisting materials: organic–organic, inorganic–organic, and inorganic–inorganic eutectics.

The requirements for phase-change materials are presented below [38].

Thermophysical Requirements:

- 1. Melting point suitable for a specific application of PCMs (between 20 and $80 \,^{\circ}$ C);
- 2. High value of:
 - (i) Melting heat.
 - (ii) Specific heat capacity.
 - (iii) Thermal conductivity of solid and liquid phases.
 - (iv) Density.
 - (v) Phase change rate.
- 3. Cyclic stability.
- 4. Low pressure of PCM vapor.
- 5. Small volume change during melting.
- 6. Homogenous structure.

Chemical requirements

- 1. Stability.
- 2. No degradation during crystallization/melting.
- 3. Reversibility of crystallization/melting.
- 4. Incombustibility.
- 5. Nontoxicity.
- 6. Explosion safety.

Economic and ecological requirements:

- 1. Low cost.
- 2. High economic efficiency.
- 3. Availability.
- 4. Ecological safety.

3. Parameters of Heat Storage Systems

This section contains estimations of parameters of PCM-based heat storage systems. Firstly, consider the possibility of usage of a PCM panel for decreasing the diary temperature oscillations in a standard living or industrial room. For the sake of definiteness, paraffin wax will be considered as a PCM. Taking into account the data presented in Table 1, let the melting (phase change) temperature of the paraffin wax $T_m = 30$ °C, specific melting heat H = 200 J/g, density $\rho = 0.75 \text{ g/cm}^3$, Specific heat capacity c = 2.1 J/g K, thermal conductivity $\kappa = 0.2 \text{ W/(m K)}$, thermal diffusivity $\alpha = 1.3 \times 10^{-3} \text{ cm}^2/\text{s}$. Let the room be a square of l = 4.7 m per side, $S = 20 \text{ m}^2$ of area, and h = 3 m of height. Estimate the heat balance in this room assuming that the outdoor (night) temperature is 20 °C lower than the inside temperature which is supposed to be $T_i = 20 \text{ °C}$. The experience indicates that for fixing the inside temperature in such a room on an acceptable level the thermal power of about $W \approx 2 \text{ kW}$ should be provided. If the wall panels contain a PCM this power is released from the panels because of the phase transition. Assuming the duration of the cold period of the day of $\tau_c = 10$ h, one obtains the estimation of the energy ε , which is necessary to store in PCM panels

$$\varepsilon = W\tau_c = 7.2 \times 10^7 \, \mathrm{J} \tag{1}$$

This energy can be stored in a PCM having the specific phase transition enthalpy of $H \approx 200$ J/g. The minimal mass of PCM M_{min} , which is necessary to store the above-mentioned energy is expressed through the quantities ε and H as follows:

$$M = \varepsilon / H = W \tau_c / H \approx 350 \text{ kg}$$
(2)

This corresponds to the volume of PCM

$$V = M/\rho \approx 4.37 \times 10^5 \text{ cm}^3 \tag{3}$$

The area of the wall panels S_p is determined as

$$S_{\rm p} = 4l^2h \approx 5.6 \times 10^5 \,\mathrm{cm}^2 \tag{4}$$

Therefore, the thickness of the PCM layer *d* in the building panel is estimated through the obvious relationship

$$d = V/S_{\rm p} \approx 0.8 \,\rm cm \tag{5}$$

The characteristic time τ required for heat propagation through the PCM layer is estimated through the relationship

$$\tau \approx d^2/\alpha \approx 500 \,\mathrm{c} \approx 8 \,\mathrm{min}$$
 (6)

Therefore, the time delay in the reply of the PCM panel on temperature oscillations is much shorter than the duration of a night. The estimations performed permit one to believe that the usage of PCM-containing panels allows saving the energy spent for heating and air conditioning residential and industrial rooms. A room whose walls contain PCM panels is well-protected from diary temperature oscillations. This protective action can be illustrated by the results of numerical calculations.

The serious problem arising from the usage of PCM relates to a rather low thermal conductivity of such materials. For this reason, the heat exchange time for elements of constructions containing PCM is usually too long. This time can be shortened either by decreasing the size of the container holding PCM or by the enhancement of the thermal conductivity of the material. One of the ways to decrease the size of PCM containers is the encapsulation of PCM into a set of miniature envelopes [2,3,29,45,46]. In this case, the characteristic heat exchange time can be shortened down to a second level by decreasing the envelop size. The drawbacks of such an approach are the additional expenditures necessary for the preparation of encapsulated material and in decreasing the specific latent energy of the encapsulated PCM with considering the mass of envelopes.

One more version of the heat storage system depleted of the above-indicated drawbacks is the water thermal accumulator (WTA) where the thermal energy is stored in PCM as a result of the passage of hot water. This results in melting PCM, which accumulates the phase transition energy. This energy can be released because of the passage of cold water through a container filled with PCM. The most appropriate configuration of WTA seems to be a set of similar modules. The configuration of the module is represented schematically in Figure 2. Each of the modules contains double concentric cylindrical tubes, where the inner tube is designed for the passage of hot or cold water while the cavity between the outer and inner tubes is filled with PCM. The inner tube of radius R_1 is fabricated from a highly thermally conductive material (for example, copper), which facilitates the thermal exchange between water and PCM. The outer tube of a radius R_2 should be fabricated from a plastic having rather low thermal conductivity, which prevents heat losses through the thermal exchange between PCM and the environment. In such a system, the characteristic heat exchange time can be shortened by increasing the inner tube radius.

The energy *E* stored in PCM as a result of the phase transition is expressed by the following relation

$$E = MH \tag{7}$$

where *M* is the mass of PCM and *H* is the specific phase transition energy. The stored energy can be extracted and used because of passing cold water through the inner tube. Cooling PCM causes the phase transition which results in heating water up to a temperature close to the phase transition point.



Figure 2. Schematic representation of a WTA module. 1—cylindrical tube of outer radius R_1 and wall thickness of d_1 for passage of hot or cool water; 2—copper envelope of the inner cylinder; 3—space between the inner and outer cylinder filled with PCM; 4—plastic envelope of inner radius R_2 and of d_2 in thickness of the outer cylinder; 5—cold water input; 6—hot water input; 7—hot water output; 8—cold water output; 9—water supply taps; 10—thermocouples.

The PCM mass is determined by the volume of the space between the outer and inner cylinders which is expressed through the radiuses of those R_1 and R_2 :

$$M = \pi (R_2^2 - R_1^2) L\rho$$
 (8)

where ρ is the density of PCM and *L* is the tube length. The characteristic heat exchange time τ is expressed by the equation

$$\tau_{he} = (R_2 - R_1)^2 / \alpha \tag{9}$$

where $\alpha = \lambda/\rho c$ is the thermal diffusivity of PCM, λ is its heat conductivity and c is the specific heat capacity.

Setting for definiteness sake the quantities $R_1 = 1$ cm, $R_2 = 2$ cm, L = 1 m and assuming the usage of paraffin wax as a PCM, one obtains in accordance with (2) for the mass of PCM embedded into one module $M_{PCM} = 716$ g. This corresponds, according to (1), to the latent energy content of the module $\varepsilon \approx 154$ kJ. This energy can be stored in PCM as a result of cooling water having the temperature exceeding the melting point by 20 °C. The characteristic heat exchange time estimated by (3) accounts for about 22 min. This time can be shortened considerably as a result of doping PCM with nanocarbon particles. Thus experiment [7] indicates that the thermal conductivity coefficient of paraffin doped with 1% (by weight) thermally reduced graphene oxide enhances by 15 times. Therefore, for such a composite, the heat exchange time is estimated as 90 c. This time determines the minimum duration of the interaction of the water flow with the PCM volume and therefore the maximum water flow velocity: $v_{max} = L/\tau \approx 1$ cm/c. The duration of passage of the water flow through the thermal accumulator τ_f is expressed through the mass of water $M_w = 1.8$ kg used for melting paraffin.

$$\tau_f = M_w / \rho v S \approx 750 \text{ s} \tag{10}$$

This time is of the same order as the characteristic heat exchange time τ_{he} determined by relation (9). Therefore, hot water has no time to transfer its thermal energy to PCM which requires the usage of a PCM with an enhanced thermal conductivity coefficient.

The character of thermal exchange between the water flow and PCM in the abovedescribed setup was modeled numerically using the code COMSOL considering the phase transition energy sink. The non-stationary heat conduction equation was resolved assuming that the thermal conductivity of the inner copper tube is infinity while the thermal conductivity of the outer polymer tube is zero. The initial water temperature was set to 90 °C while the initial temperature of PCM was set to 20 °C. The results of the simulation are presented in Figure 3 in terms of the dependences of the PCM temperature on the longitudinal and transverse coordinates at various points in time. As is seen, the calculation results are compatible qualitatively with the above-performed estimations. The calculations indicate that at the water flow velocity of 10 cm/s the full melting time of paraffin accounts for about 250 s, which corresponds to the mass of passed water about 1.7 kg. As is seen, the radial dependence of the temperature is relatively slow practically during all the time of the heat exchange.



Figure 3. Cont.



Figure 3. Longitudinal and transverse temperature profiles in PCM calculated for various points in time τ after starting the water flow: (a) $\tau = 10$ s; (b) $\tau = 50$ s; (c) $\tau = 150$ s; (d) $\tau = 250$ s. Different lines correspond to various distances from the axis: -r = 7.5 mm; -...r = 8.5 mm; -..r = 9.5 mm; -..r = 10.5 mm; -..r = 10.5 mm; -..r = 12.5 mm; -..r = 13.5 mm.

4. Thermal Conductivity of Carbon Nanoparticles

Carbon nanoparticles such as carbon nanotubes (CNT) and grapheme flakes have very high thermal conduction coefficients and can be considered as a proper dopant to enhance that of PCM. The thermal conduction of CNTs is determined by phonons so that the role of electrons in conduction is negligible [43,47,48]. Short nanotubes (less than ~1 μ m) usually do not have defects and both charge and heat transport in them have a ballistic character. In the case of ballistic heat, transport phonons propagate through a medium without scattering, so that the characteristic phonon mean free path relating to the scattering on

phonons and structural defects exceeds the length of the nanotube. The simplest description of ballistic phonon thermal conductivity corresponds to a high-temperature limit, which takes place at $\hbar \omega \ll T$ (ω is the characteristic phonon frequency, T is the temperature). In this case, the thermal conductance of each phonon channel is determined by the quantum magnitude G_{th} , which has the form [48].

$$G_{th} = \frac{\pi^2 k^2 T}{3h} = 9.46 \times 10^{-13} \left(\frac{W}{K^2}\right) T \tag{11}$$

This corresponds to the quantity $G_{th} = 2.84 \times 10^{-10}$ W/K at room temperature. The thermal conductance of a CNT is expressed as the product of the quantum conductance G_{th} and the total number of phonon channels N_p in the nanotube. The latter is a double number of atoms in a unit cell 2*N*, where *N* is expressed through the chirality indices (*n*, *m*) of the nanotube as [49–51].

$$N_p = \frac{2(n^2 + m^2 + nm)}{d_R}$$
(12)

Here, d_R is the greatest common divisor of (2n + m) and (2m + n). For a CNT having the armchair structure and chirality indices (n, n), $d_R = n$ and $N_p = 6n$. For example, a single-walled (10, 10) CNT (diameter d = 1.4 nm) has $N_p = 120$ phonon channels, while a (200, 200) CNT (diameter d = 27.5 nm) has $N_p = 2400$ phonon channels. Therefore, the ballistic thermal conductance of (10, 10) and (200, 200) CNTs amounts to $120G_{th}$ and $2400G_{th}$, respectively. This corresponds to the room temperature thermal conductivity of CNT of $L = 1 \mu m$ in length $\lambda = G_{th}N_p(L4/\pi d^2) = 5000$ W/m K for (10, 10) CNT and $\lambda = 266$ W/m K for (200, 200) CNT.

The thermal conductivity of CNTs decreases abruptly as the nanotube's length *L* exceeds the characteristic mean free path l_p of photons due to the scattering of phonons on structural defects and admixture centers. The role of defects can be taken into account through the correcting factor $k_d = \lambda/(L + \lambda)$, so the thermal conductivity coefficient of a CNT is approximately expressed by the following relation [43]

$$A = G_{th} N_p \frac{L}{\pi d^2} \frac{l_p}{L + l_p}$$
(13)

As is seen, the thermal conductivity of long CNTs does not depend on their length and is proportional to the phonon mean free path. The typical value of the thermal conductivity of short nanotubes is about 5000 W/m K. This conclusion is confirmed by the results of many experiments [48,49].

Similar to CNTs, the thermal conductivity of graphene flakes depends on both the content of structural defects and the geometry of a sample. This parameter was measured using the temperature dependence of grapheme Raman frequencies [52,53]. According to this approach, a laser beam of a specified power is focused onto the middle of a single-layer graphene sheet suspended between two supports. The size of the irradiated spot is 0.5 ± 1 mm, and the temperature increase in the spot amounts to several dozen Kelvins. The temperature of the heated site of graphene is determined by the temperature shift in the position of the G peak in the Raman spectrum. At moderate heating, the increase in temperature depends linearly on the laser power, and the coefficient in this dependence is proportional to the thermal conductivity of graphene.

The experimental setup [52,53] is shown schematically in Figure 4. A set of longitudinal trenches 300 nm in depth and up to 5 mm in width were fabricated by ion etching on the surface of a Si/SiO_2 substrate. Graphene sheets produced by the micromechanical exfoliation of highly oriented pyrolytic graphite were applied onto the substrate in large numbers. Then, elongated graphene samples bridging the two sides of the trench and close in form to a rectangle were selected by means of a Raman microspectrometer. In so doing, the graphene sheets under investigation were put into thermal contact with the graphite particles that also resided on the substrate surface. These particles absorb the heat released

on irradiation of the graphene sheet by a focused beam of an Ar-ion laser ($\lambda = 0.48 \mu m$). The size of the focal spot is about 0.5 μ m; however, the size of the hot region is increased to 1 μ m due to electron diffusion. The measurements yielded magnitudes of the thermal conductivity coefficient ranging between 4840 and 5300 W/m K. The processing of the experimental data also allowed the estimation of the magnitude of the phonon mean free path with respect to the scattering: $l_p \approx 775$ nm. Hence, l_p turned out to be much less than the characteristic size (5 \pm 10 μ m) of the graphene sample, which demonstrates the prevailing role of the diffusion mechanism of heat transport over the ballistic one.



Figure 4. Schematic of the experimental setup for measuring the thermal conductivity of graphene [52,53].

The measurements indicate that the thermal conduction coefficient of an individual graphene layer exceeds by more than two times the appropriate value for crystalline graphite: $\kappa \approx 2000$ W/m K. Therefore, the thermal conductivity of a 2D hexagonal structure (graphene) exceeds notably that of a 3D structure consisting of graphene layers. Transition from a 2D to a 3D structure occurs upon increasing the number of graphene layers, which should be accompanied by a lowering of the thermal conduction coefficient. Such a behavior can be attributed to an additional mechanism of phonon scattering related to the interaction between neighboring layers. This behavior has been studied experimentally by the authors of Ref. [54], who utilized for this aim the Raman spectroscopy method in the manner described above. In this case, Si/SiO_2 wafers with a set of parallel trenches 300 nm in depth and up to 5 mm in width were also used. The heat delivered to the graphene sheet by laser irradiation was removed through thin metal pads deposited near the edges of the trenches. Few-layer graphene samples were produced by micromechanical exfoliation of pyrolytic graphite. The number of layers in the samples under investigation was determined through processing the Raman spectrum [55]. The longitudinal size of the suspended part of the graphene sheet ranged between 5 and 16 mm. The thermal conductivity of the graphene samples was determined by fitting the measured temperature shift of the G Raman peak $(\approx 1579 \text{ cm}^{-1})$ under the action of laser irradiation to the solution of the relevant heat conduction equation for the sample by the finite element method. The dependence of the thermal conduction coefficient of few-layer films on the number of graphene layers measured by the authors of Ref. [54] is presented in Figure 5. These data have been reduced to the common lateral size of 5 mm in order to exclude the dependence of the thermal conduction coefficient on this parameter. The results of simulations performed by various methods are also presented, as well as the result of measuring (for comparison) the thermal conductivity for individual single-layer graphene. As may be seen, the thermal conductivity of a few-layer graphene structure approaches that of crystalline graphite already when the number of layers reaches four.



Figure 5. Dependence of the longitudinal thermal conductivity of few-layer graphene films on the number of layers [54]. The dashed lines indicate the limits of spreading the thermal conductivity of crystalline graphite; diamonds: calculated results considering all the possible phonon scattering mechanisms, excluding the scattering on defects; triangles: calculations [56–59] for multilayer graphene structures taking into account the roughness; square: maximum magnitude [53]; dots: averaged value for a suspended graphene sheet 5 mm in length. All the measurements were performed at room temperature.

An alternative approach to measuring the thermal conduction coefficient of graphene was applied in Ref. [60], where the graphene samples were synthesized by the reduction of graphene oxide that was produced using the standard Hummers method [61]. The graphene oxide reduction procedure was performed in flowing nitrogen at a temperature of 450 °C and lasted from 5 to 60 min. The thermal conductivity of the reduced graphite samples was determined by combining the results of measuring the temperature of the sample heated by electrical current with the solution of a 1D heat conduction equation. The temperature of the sample was measured by means of a Pt thermocouple.

The thermal conductivity of samples was measured under vacuum conditions at a residual gas pressure of less than 0.03 Torr. The measurement device included a SiN substrate on which the longitudinal silicon pads used as contacts were placed. The distance between the pads ranged between 0.5 and 3 mm. A graphene sample was applied to the substrate in such a way that the electrical and thermal contacts with the pads were maintained. In one measurement configuration, a graphene sheet was suspended between those pads not having contact with the substrate, while in another one a graphene sheet partially lay on the substrate. The structure of the measuring system permitted taking measurements of both the thermal conductivity and the electrical conductivity of the sample simultaneously. The results of these measurements at room temperature are given in Table 4 for four samples. These samples differ in size, contact resistance, and the duration *t* of thermal treatment at reduction of graphene. Furthermore, samples 2 and 3 were suspended, while samples 1 and 4 were in contact with the substrate surface.

The measurement results presented in Table 4 reveal a notable dependence of the transport coefficients of graphene on the duration of the thermal treatment of samples: the more prolonged the treatment duration, the higher the coefficients of thermal and electrical conductions of the sample. While the mechanisms of the electric conduction and thermal conduction are different (electrons and phonons), the samples having an enhanced electric conductivity also demonstrate enhanced thermal conductivity. This is explained by the removal of oxygen atoms from the graphene surface because of thermal treatment. Oxygen adducts on the graphene surface determine the mechanism of electron and phonon scattering, and their presence lowers the magnitude of the relevant transport

coefficients. However, even thermal treatment for one hour does not allow the total removal of oxygen. Therefore, in this case, both the thermal conduction coefficient and the electrical conductivity of graphene remain several orders of magnitude lower than those for graphene samples produced by either the mechanical exfoliation of graphite or the CVD method. This permits the conclusion of high sensitivity of the transport coefficients of graphene samples to both the method used for their production and synthesis conditions.

Sample	Thermal Conductivity κ, W/m K	Electrical Conductivity σ , S/m	Duration of Annealing, min	Contact Resistance, kΩ
1	2.87	62.2	60	120
2	0.87	6.21	5	2
3	0.14	6.57	5	130
4		19.5	20	300

Table 4. Transport characteristics of thermally reduced graphene samples [60].

Recent experiments (see, for example, [62–64]) indicate that thermally reduced graphene oxide can possess much higher transport characteristics than those shown in Table 4. Therewith the experiments performed show that reliable, well-reproducible results can be obtained only at a rather low rate of heating. Thus, heating samples with a rate higher than 1 °C/s results in non-controllable explosive-like destruction of the material. For this reason, the rate of heating the furnace from a room temperature up to 200 °C was 2 °C/min, while the rate of the subsequent heating up to the annealing temperature was ~1 °C/s. The duration of the thermal treatment was 10 min at all the temperatures.

The thermal treatment of graphene oxide samples results in the removal of oxygen, which causes a decrease in the density of samples. Figure 6 presents the dependence of the graphite samples density on the annealing temperature. Figure 7 presents the dependence of the electric conductivity of thermally reduced graphene oxide on the annealing temperature measured by the authors of [63,64]. As is seen, the density decreases by about 3.5 times as the annealing temperature enhances from 100 up to 800 °C. The decrease in the density of the samples means that the average distance between graphene oxide flares increases approaching the value of 1.66 nm at the annealing temperature of 800 °C. This value exceeds the inter-layer distance in crystalline graphite by 4.5 times, therefore, one can believe that the thermally treated graphene oxide samples have transport characteristics close to those of graphene. This is confirmed by the results of measurement of the dependence of the electric conductivity of graphene oxide samples on the thermal treatment temperature [63,64] presented in Figure 7.



Figure 6. Dependence of the density of partially reduced GO on the annealing temperature [63,64].



Figure 7. Dependence of the conductivity of reduced GO samples on the annealing temperature. The points have been obtained as a result of averaging over many samples and several magnitudes of the applied voltage [63,64].

As is seen, the removal of oxygen through the thermal treatment of graphene oxide samples promotes not only enhancement in the average distance between graphene oxide flakes but also an enhancement of their electrical conductivity. The maximum reached value of the conductivity of the reduced GO (~3500 S/m) is about an order of magnitude lower than the reference value for graphite. However, taking into account that the distance between neighboring graphene oxide flakes is about 4.5 times larger than that of graphite, one can conclude that the conductivity of the material accounting for one graphene layer is only twice lower than that for graphite. Therefore, thermally reduced graphene oxide possesses a layer structure with an average inter-layer distance of about 1.5 nm and the conductivity (accounted for one layer) close to that for graphite. At such a distance, the interaction between the neighboring layers is negligible so it is natural to conclude that the layers involved in such a structure are close to graphene in their characteristics, annealing results in the thermal reduction of GO fragments, which lose added oxygen and transform to a conducting state. The conductivity of such a material has a percolation nature and is determined by the resistance of contacts between neighboring fragments, which decreases as the applied voltage enhances. The data presented in Table 4 demonstrate a rough proportionality between the thermal conduction and electric conduction coefficient. It can be used for the estimation of the thermal conduction coefficient of the thermally reduced graphene oxide samples based on the measured electrical conductivity of those measured in [63,64] and presented in Figure 7. The averaged ratio σ/κ determined on the basis of data of Table 4 accounts \approx 25.2 S K/W. Using this ratio and the data shown in Figure 7, one finds that the thermal conduction coefficient of thermally reduced graphene oxide samples should reach $\approx 140 \text{ W/m K}$.

The thermal conductivity of an individual graphene sample is determined by the character of phonon propagation along the graphene plane. In this case, the phonon mean free path depends on such factors as the graphene size, the type and concentration of defects, and the occurrence of neighboring structures, as is the case in crystalline graphite or in a film consisting of several graphene layers. In the absence of those factors, the characteristic phonon mean free path for elastic scattering is determined by the phonon interaction processes (Umklapp processes), and their inclusion into consideration results in an increasing dependence of the thermal conduction coefficient on the graphene size. The specific shape of this dependence is determined by the Grüneisen parameter γ , which describes the effect of changing the volume of a crystal lattice on its dependence on its vibrational properties. Figure 8 presents the dependences of the thermal conductivity of defectless graphene sheet on its size [65] calculated for different values of the Grüneisen parameter (for longitudinal γ_{LA} and transverse γ_{TA} vibrational modes). As is seen, the thermal conductivity is a monotonically increasing function of the graphene sheet size independently of the choice of the Grüneisen parameter. The room-temperature magnitude



of the thermal conductivity for $L = 10 \ \mu m$ turned out to be close to 4000 W/m K which corresponds approximately to the experimental data (shown by the point).

Figure 8. Dependences of the room temperature thermal conductivity *k* of a rectangular defectless graphene sheet on size *L* calculated for different values of the Grüneisen parameter for longitudinal γ_{LA} and transverse γ_{TA} vibrational modes [65].

The heat transport in defectless graphene is hindered by the phonon-phonon scattering (umklapp process). The role of this process increases as the temperature enhances because the number of phonon modes enhances with the rise of the temperature. Therefore, the temperature dependence of the thermal conductivity of defectless graphene is a decreasing function. Results of calculation of this function performed by the authors [65] for various graphene sheet size *L* are shown in Figure 9. The results of calculations are in satisfactory agreement with experimental data (shown by point).



Figure 9. Temperature dependences of the thermal conductivity *k* of a rectangular defectless graphene sheet of various size [65].

The structure of real graphene samples can contain both intrinsic defects and, depending on the method of preparation, various surface functional groups. These defects contribute to the probability of acoustic phonon scattering, whereas the thermal conduction coefficient of real graphene samples depends on the number density of the most probable defects. This dependence was evaluated both by utilizing MD simulations and through Boltzmann kinetic equation calculations. Thus, the results of Non-Equilibrium Molecular Dynamic (NEMD) calculations [66,67] indicate an abrupt decrease in the thermal conductivity as the defect number density increases. In this regard, single and multiple carbon vacancies, OH-group adducts, and the roughness of the graphene sheet were considered as defects. Along with the NEMD method, the dependences of the thermal conductivity of graphene on the number density of OH groups and carbon vacancies were calculated by means of the Boltzmann kinetic equation. The results of calculation [66] of the dependence of the thermal conductivity coefficient on the defect number density are presented in Figure 10. The results obtained by the two methods are in qualitative agreement with each other and demonstrate that the defect number density promoting a decrease in the thermal conductivity by a factor of 2 is about 1% at room temperature for OH groups (Figure 10b) and about 0.1% for the case of vacancies (Figure 10a). Notice that the dependences of the thermal conduction coefficient on the defect number density calculated in the above-cited works are in qualitative agreement with the results of simulations for single-walled carbon nanotubes, which also point to a decrease in the thermal conductivity as the defect number density increases [68].



Figure 10. The thermal conductivity of a defective graphene sheet $L = 1 \ \mu m$ in length as a function of the concentrations of vacancies (**a**), and OH groups (**b**) calculated using the NEMD method and the Boltzmann kinetic equation method with two types of phonon distribution statistics (classic and quantum Bose) [66].

5. Thermal Conduction of Polymer Composites Doped with Carbon Nanoparticles

As it was mentioned above, the effective usage of PCM as a basis of thermal accumulating systems is possible if the thermal conductivity of PCM can be enhanced by several times. This can be reached as a result of doping PCM with nanocarbon particles the thermal conductivity of which exceeds that of PCM by 4–5 orders of magnitudes. The electrical conduction of polymer materials doped with carbon nanotubes has been studied in a lot of publications some of which were reviewed in articles [44,69]. The electric conduction in such composites has a percolation character in accordance with which the charge transport occurs through a limited number of percolation paths formed by the nanotubes contacting with each other. The heat transport in composites doped with carbon nanoparticles proceeds by a similar mechanism, however, this phenomenon has been studied at a rather lower degree.

The thermal conductivity of a polymer material doped with carbon nanoparticles is determined by several factors [70], the most important among which are (1) the characteristics of the particles used (defect content, the geometry, aspect ratio), (2) the dispersion of carbon nanoparticles within the composite, (3) the percent content loading of particles (volume% or weight%), and (4) the interfacial contact between the polymer matrix and the nanocarbon filler. The heat transport in both polymer matrix and nanocarbon particles is provided by phonon propagation. A multitude of interfaces connected doped particles with molecules of the composite hinders the heat propagation through the composite because the interfaces scatter phonons. Mechanisms of heat conduction in polymer-based composites and recent advances in the experimental and calculation research in the field have been reviewed in [71,72].

One distinguishes composites with a random orientation of graphene flakes and that with an ordered orientation. Composites of the first type are comparatively easy in preparation based on standard approaches such as solution mixing, melt mixing, in-situ polymerization, etc. [73–80]. There have been published a lot of experiments indicating a notable enhancement of the thermal conductivity of polymer composites doped with graphene flakes with a random orientation. The results of these experiments are presented in Table 5 [73]. The degree of influence of a dopant on the thermal conductivity of a composite is characterized by the factor Thermal Conductivity Enhancement (TCE) which corresponds to the enhancement of the thermal conductivity per 1% of dopant.

Table 5. Parameters of polymer composites with a random orientation of graphene [73].

Polymer	Graphene Content, wt%	Thermal Conductivity, W/m K	TCE, % per wt% of Graphene	Preparation Method	Surface Preparation Method	Ref.
Py-PGMA-GNS/epoxy	3.8	1.91	225	In-situ polymerization	Non-covalent modification	[81]
f-GFs/epoxy	10	1.53	66.5	In-situ polymerization	Non-covalent modification	[82]
GnP-C750/epoxy	5	0.45	23.8	In-situ polymerization	no	[83]
DGEBA-f-GO/epoxy	4.64	0.72	52.3	In-situ polymerization	no	[84]
GS@Al ₂ O ₃ /PVDF	40	0.586	4.8	Solution mixing	Coated by alumina nanoparticles	[85]
Al ₂ O ₃ @ GNP/epoxy	12	1.49	56.4	Solution mixing	Coated by alumina	[86]
ApPOSS-graphene/ epoxy	0.5	0.348	115.8	Solution mixing	Covalent modification	[87]
GNP/PBT	20	1.98	61	In-situ polymerization	no	[88]
GNPs/PPS	37.8	4.414	49	Melt mixing	Covalent modification	[89]
PI/SiCNWs-GSs	7	0.577	21	Solution mixing	no	[90]
GP/SR	0.72	0.3	69.4	Mechanical blending	Covalent modification	[91]
PA6/graphene-GO	10	2.14	56.9	In-situ polymerization	Non-covalent modification	[92]
GNP/epoxy	25	2.67	49.4	Solution mixing	No	[93]
PVDF/FGS/ND	45	0.66	3.9	Solution mixing	no	[94]
ApPOSS-graphene/epoxy	0.5	0.348	115.8	Solution mixing	Covalent modification	[95]

	Table 5. Cont.					
Polymer	Graphene Content, wt%	Thermal Conductivity, W/m K	TCE, % per wt% of Graphene	Preparation Method	Surface Preparation Method	Ref.
IL-G/PU	0.608	0.3012	55.9	In-situ polymerization	Non-covalent modification	[96]
PA/TCA-rGO	5	5.1	357.8	Melt mixing	Covalent modification	[97]
BE/graphene	2.5	0.542	73.7	Solution mixing	Covalent modification	[98]
GNPs/silicone	16	2.6	49.7	In-situ polymerization	no	[99]

Abbreviations: Py-PGMA-GNS/epoxy: Pyrene-end poly(glycidyl methacrylate)-graphene nanosheet/epoxy composite; f-GFs/epoxy: Non-covalently functionalized graphene flakes/epoxy composite; GnP-C750/epoxy: Graphene nanoplatelets (sizes < 1 μ m)/epoxy composite; DGEBA-f-GO/epoxy: Diglycidyl ether of bisphenol-A functionalized graphene oxide/epoxy composite; GS@Al₂O₃/PVDF: Alumina-coated graphene sheet/poly(vinylidene fluoride) composite; Al₂O₃@GNP/epoxy: Alumina nanoparticles decorated graphene nanoplatelets/epoxy composite; GNP/PBT: Graphene nanoplatelet/polybutylene terephthalate composite; GNPs/PPS: Graphene nanoplatelets/polybutylene terephthalate composite; GNPs/PPS: Graphene nanoplatelets/epoxy composite; GP/SR: Graphene/silicone rubber; PA6/graphene-GO: Polyamide-6/graphene-graphene oxide composite; GNP/epoxy: Graphene nanoplatelets/epoxy composite; NDP/FGS/ND: Poly(vinylidene fluoride)/functionalized graphene sheets/nanodiamonds composite; IL-G/PU: 1-allyl-methylimidazolium chloride ionic liquid modified graphene/polyurethane composite; PA/TCA-rGO: Titanate coupling agent modified reduced graphene/polyamide composite; BE/graphene: Bio-based polyester/graphene composite; GNPs/silicone: Graphene nanoplatelets/silicone composite; BE/graphene: Bio-based

One should note that the preparation of a polymer-based composite doped with carbon nanoparticles presents a great challenge for researchers. An enhancement of the thermal conductivity of a composite because of doping with carbon nanoparticles can be reached under the condition of a homogeneous distribution of a carbon filler over the matrix volume. The attainment of such a distribution is hindered due to a trend of carbon nanoparticles to aggregation. For this reason, various techniques were utilized for the preparation of polymer-based nanocomposites doped with carbon particles. A systematic investigation of the dispersion degree of carbon nanotubes (CNT) in a bisphenol F-based epoxy resin in dependence on the method of composite preparation has been performed by the authors of Ref. [100]. The CNTs used were 1–6 nm in diameter and a few microns in length. Composites were prepared using such dispersion techniques as high-speed dissolver, roll-milling, ultrasonication, etc. The degree of homogeneity of the filler was controlled during the entire processing cycle by means of optical microscopy. There has been shown that the standard roll-mill technique not only enhances the dispersion of CNTs into an epoxy matrix but also that promotes the re-agglomeration of CNTs during the preparation. Polymer-based composites doped with CNT demonstrate a several times enhanced thermal conductivity at a filler concentration of about 10%.

Much higher enhancement in the thermal conductivity has been obtained for composites doped with graphene nanoflakes (GNF). Thus, the authors of [101] studied the thermal conductivity of the composite on the basis of poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF/HFP). The GNF/PVDF-HFP composite films were produced using hot mixing of the components in the presence of a solvent, molding, and subsequent solvent evaporation). GNF were dispersed in *N*,*N*-dimethylformamide (DMF) by sonication at 35 °C for 30 min. This dispersion was inserted by parts into the solution of PVDF-HFP in DMF under magnet stirring. Then the mold was thermally treated in an oven at 90 °C for 24 h to remove DMF. The results of measuring the thermal conduction coefficient vs. the filler concentration are presented in Figure 11. As is seen, the thermal conduction enhancement coefficient (TCE) reaches 10,000% at a filler loading 20 weight%.



Figure 11. Thermal conductivity and thermal conductivity enhancement as a function of graphene nanoflake (GNF) wt% [101]. The experimental points correspond to the content 0, 6, 10 and 20 wt%. The parameters of the linear approximation of the experimental data and the regression value (R²) are shown on the picture.

The filler concentration, filler size, and temperature dependences of the thermal conductivity of graphene nanocomposites were studied theoretically by the authors [102] via an effective-medium approximation based on Maxwell's far-field matching at a microscopic level. The results are in close agreement with the experimental observations over the average filler size from 200 to 1000 nm and over the temperature from 300 to 360 K, respectively. Figure 12 presents the comparison of the dependences of the thermal conductivity of the polymer-based composite on the volume concentration of the graphene dopant calculated in [102] for various sizes of graphene flakes with the relevant experimental data. These dependences have a form typical for the percolation thermal conductivity.



Figure 12. The thermal conductivity of the nanocomposite vs. the volume concentration of the graphene nanofiller calculated in [102] and measured for different graphene size in various works: 1—[103]; 2—[104]; 3—[105]; 4—[83].

Figure 13 shows the temperature dependences of the thermal conductivity of polymerbased composite doped with few-layer graphene particles calculated in [92] and measured in [97] for the volume dopant loading 10%. The calculations were performed for the average graphene lateral dimension 2000 nm; the average graphene thickness 1.4 nm; the thickness of interlayer between the neighboring graphene flakes 0.14 nm. As is seen, both calculated and measured thermal conductivity demonstrate a slightly increasing temperature dependence which is typical for percolation phonon thermal conduction.



Figure 13. Temperature dependences of epoxy-based composite doped with 10% (volume) few layer graphene flakes [102]. - - - calculation without graphene size effect; —— calculation with graphene size effect; experimental points—[106].

A careful study of the thermal conductivity of graphene doped polymer-based composites has been performed by the authors of [70] who prepared a set of composite samples based on polymer PVDFHEP. The polymer was doped with 98.5% pure graphene flakes in weight percentages wg varying between 0.1% and 50%. The graphene flakes have dimensions ~(7 × 3.5 × 0.001) µm³. The results of measuring the thermal conductivity coefficient of composites at various graphene content are summarized in Table 6. As is seen, inserting 1% (weight) graphene results in the enhancement of the thermal conductivity coefficient as much as 15 times.

Table 6. Thermal conductivity of polymer-based samples with various graphene loading [70].

wg, %	0	1	6	10	20	25	33	50
K, W/m K	0.22	3.24	7.95	16.0	24.5	36.3	38.1	57.51

Along with carbon flakes, carbon nanotubes can be also used as an effective dopant for enhancement of the thermal conductivity of polymer-based composites. In this relation the article [107] should be mentioned, where the effects of doping polymer matrix with expanded graphite particles (EGPs) and multi-walled carbon nanotubes (MWCNTs) on the thermal conductivity of composites are compared. A PCM matrix was used in the mixture of paraffin (melting temperature 20–25 °C; latent heat 122.6 J/g), high-density polyethylene (HDPE), and styrene-butadiene copolymer (SBS). MWCNTs have an average diameter of 10 nm and an average length of 10 μ m. The experiments performed have shown that both EGPs and MWCNTs increase the thermal conductivity of PCMs, while EGPs demonstrate a greater thermal conductivity improvement than MWCNTs. The conductivity of EGP-filled PCM reached 0.574 W/mK at 9 wt%, while that of MWCNT was just 0.372 W/mK at the same loading.

Figure 14 presents the dependences of the measured thermal conductivity of a paraffinbased PCM doped with a single filler (MWCNT) and expanded graphite particles (EGP) (a) and hybrid filler (EGP/MWCNT) (b) on the filler content. The measured dependences demonstrate a synergistic effect in the enhancement of the thermal conductivity. Thus, when the EGP/MWCNT ratio was 8:2, the most significant thermal conductivity enhancement to the SSPCM was obtained. The thermal conductivity was 0.674 W/mK, 288% that of the SSPCM and 117% that of 9 wt% EGP-filled SSPCM. The advantage of hybrid filler is in (1D) MWCNT bridges connecting 2D planar EGP. Seemly EGP-MWCNT junctions have a lower thermal resistance compared to that of EGP-EGP and MWCNT-MWCNT junctions.



Figure 14. Thermal conductivities (at 35 °C) of SSPCM filled with (**a**) single filler and (**b**) hybrid filler [107].

6. Conclusions

The usage of PCMs in the building trade permits one to limit the level of energy production and consumption, which offers a possibility to lower the negative impact of the industry on the environment and terrestrial climate. The wide spread of PCMs is hindered by a rather low thermal conductivity of these materials. This drawback can be overcome by doping PCMs with nanocarbon particles for which the thermal conductivity coefficient exceeds that for PCMs by 4-5 orders of magnitude. Due to a rather complicated geometry of nanocarbon particles, the theoretical determination of the thermal conductivity coefficient of polymer-based composites doped with them seems to be hardly possible so the main source of reliable data on this subject is experimentation. By now, a large number of experimental works have been published where the thermal conductivity coefficients of polymer composites doped with carbon nanoparticles were measured. The data obtained are characterized by a notable spread but all of them demonstrate a considerable enhancement of the thermal conductivity due to nanocarbon doping. However, the effect of doping polymers with nanocarbon particles on the thermal conductivity of a material depends critically on the method of preparation of composite. This is caused by a trend of carbon nanoparticles toward aggregation, which prevents a homogeneous distribution of the filler over the matrix volume. Besides that, the wide spread of composites in the building industry and other fields is hindered by a rather high production cost of carbon nanoparticles such as carbon nanotubes and graphene. The development of methods of large-scale production of nanocarbon materials with a decreased production cost should stimulate the usage of PCMs with enhanced thermal conductivity in the building industry, in thermal accumulating systems, for temperature stabilization of big computer systems, etc.

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References

- Sharifi, N.P.; Shaikh, A.A.N.; Sakulich, A.R. Application of phase change materials in gypsum boards to meet building energy conservation goals. *Energy Build.* 2017, 138, 455–467. [CrossRef]
- Medina, M.A.; King, J.B.; Zhang, M. On the heat transfer rate reduction of structural insulated panels (SIPs) outfitted with phase change materials (PCMs). *Energy* 2008, 33, 667–678. [CrossRef]
- 3. Vicente, R.; Silva, T. Brick masonry walls with PCM macrocapsules: An experimental approach. *Appl. Therm. Eng.* **2014**, *67*, 24–34. [CrossRef]
- 4. Peippo, K.; Kauranen, P.; Lund, P. A multicomponent PCM wall optimized for passive solar heating. *Energy Build.* **1991**, 17, 259–270. [CrossRef]
- Kenisarin, M.; Mahkamov, K. Passive thermal control in residential buildings using phase change materials. *Renew. Sustain.* Energy Rev. 2016, 55, 371–398. [CrossRef]
- 6. Fang, Y.; Niu, J.; Deng, S.S. Numerical analysis for maximizing effective energy storage capacity of thermal energy storage systems by enhancing heat transfer in PCM. *Energy Build.* **2018**, *160*, 10–18. [CrossRef]
- Abdulrahman, R.S.; Ibrahim, F.A.; Dakhil, S.F. Development of paraffin wax as phase change material based latent heat storage in heat exchanger. *Appl. Therm. Eng.* 2019, 150, 193–199. [CrossRef]
- 8. Li, W.; Qu, Z.; He, Y.; Tao, Y. Experimental study of a passive thermal management system for high-powered lithium ion batteries using porous metal foam saturated with phase change materials. *J. Power Sources* **2014**, 255, 9–15. [CrossRef]
- 9. Zhu, L.; Yang, Y.; Chen, S.; Sun, Y. Numerical study on the thermal performance of lightweight temporary building integrated with phase change materials. *Appl. Therm. Eng.* **2018**, *138*, 35–47. [CrossRef]
- Zhu, N.; Ma, Z.; Wang, S. Dynamic characteristics and energy performance of buildings using phase change materials: A review. Energy Convers. Manag. 2009, 50, 3169–3181. [CrossRef]
- 11. Kusama, Y.; Ishidoya, Y. Thermal effects of a novel phase change material (PCM) plaster under different insulation and heating scenarios. *Energy Build*. **2017**, *141*, 226–237. [CrossRef]
- 12. Wang, S.-M.; Matiašovský, P.; Mihálka, P.; Lai, C.-M. Experimental investigation of the daily thermal performance of a mPCM honeycomb wallboard. *Energy Build.* **2018**, *159*, 419–425. [CrossRef]
- 13. Borodulin, V.Y.; Nizovtsev, M.I. Heat-inertial properties of walls of lightweight thermal insulation with phase change materials. *J. Phys. Conf. Ser.* **2018**, 1105, 012108. [CrossRef]
- 14. Zalba, B.; Marín, J.M.; Cabeza, L.F.; Mehling, H. Free-cooling of buildings with phase change materials. *Int. J. Refrig.* 2004, 27, 839–849. [CrossRef]
- 15. Kandasamy, R.; Wang, X.-Q.; Mujumdar, A.S. Application of phase change materials in thermal management of electronics. *Appl. Therm. Eng.* **2007**, *27*, 2822–2832. [CrossRef]
- 16. Gharbi, S.; Harmand, S.; Ben Jabrallah, S. Experimental comparison between different configurations of PCM based heat sinks for cooling electronic components. *Appl. Therm. Eng.* **2015**, *87*, 454–462. [CrossRef]
- 17. Temirel, M.; Hu, H.; Shabgard, H.; Boettcher, P.; McCarthy, M.; Sun, Y. Solidification of additive-enhanced phase change materials in spherical enclosures with convective cooling. *Appl. Therm. Eng.* **2017**, *111*, 134–142. [CrossRef]
- 18. Kenisarin, M.M. Short-term storage of solar energy. 1: Low temperature phase-change materials. Appl. Sol. Energy 1993, 29, 48-65.
- 19. Royon, L.; Karim, L.; Bontemps, A. Optimization of PCM embedded in a floor panel developed for thermal management of the lightweight envelope of buildings. *Energy Build*. **2014**, *82*, 385–390. [CrossRef]
- 20. Chiu, Y.-J.; Yan, W.-M.; Chiu, H.-C.; Jang, J.-H.; Ling, G.-Y. Investigation on the thermophysical properties and transient heat transfer characteristics of composite phase change materials. *Int. Commun. Heat Mass Transf.* 2018, *98*, 223–231. [CrossRef]
- 21. Tokuç, A.; Başaran, T.; Yesügey, S.C. An experimental and numerical investigation on the use of phase change materials in building elements: The case of a flat roof in Istanbul. *Energy Build.* **2015**, *102*, 91–104. [CrossRef]
- 22. Ho, C.J.; Chen, C.P.; Lai, C.-M. The effects of geometric parameters on the thermal performance of a rectangular natural circulation loop containing PCM suspensions. *Numer. Heat Transf. Part A Appl.* **2016**, *70*, 1313–1329. [CrossRef]
- 23. Vasil'ev, E.N.; Derevyanko, V.A. The dynamics of phase changes in a heat storage of thermal control system for onboard radio-electronic equipment. *Thermophys. Aeromech.* **2018**, *25*, 461–467. [CrossRef]
- 24. Nizovtsev, M.I.; Borodulin, V.Y.; Letushko, V.N.; Terekhov, V.I.; Poluboyarov, V.A.; Berdnikova, L.K. Heat transfer in a phase change material under constant heat flux. *Thermophys. Aeromech.* **2019**, *26*, 313–324. [CrossRef]
- 25. Kozak, Y.; Ziskind, G. Novel enthalpy method for modeling of PCM melting accompanied by sinking of the solid phase. *Int. J. Heat Mass Transf.* 2017, *112*, 568–586. [CrossRef]
- 26. Usachev, S.M.; Pertsev, V.T.; Khav'yarimana, S. Heat storage materials for building materials and structures. *Nauchn. Zh. Stroit. Arkhit.* **2018**, *2*, 68–75. (In Russian)
- 27. Aymbetova, I.; Suleymenov, U.; Kambarov, M.; Kalshabekova, E.; Ristavletov, R. Thermophysical properties of phase transparent heat-storing materials used in construction. *Adv. Curr. Nat. Sci.* **2018**, *1*, 9–13. [CrossRef]
- 28. Abhat, A. Low temperature latent heat thermal energy storage: Heat storage materials. Sol. Energy 1983, 30, 313–332. [CrossRef]
- 29. Bendic, V.; Dobrotă, D. Theoretical and Experimental Contributions on the Use of Smart Composite Materials in the Construction of Civil Buildings with Low Energy Consumption. *Energies* **2018**, *11*, 2310. [CrossRef]
- 30. Bendic, V.; Dobrotă, D.; Dobrescu, T.; Enciu, G.; Pascu, N. Rheological Issues of Phase Change Materials Obtained by the Complex Coacervation of Butyl Stearate in Poly Methyl Methacrylate Membranes. *Energies* **2019**, *12*, 917. [CrossRef]

- 31. Bendic, V.; Dobrotă, D.; Simion, I.; Bălan, E.; Pascu, N.-E.; Tilina, D.I. Methods for Determining the Thermal Transfer in Phase-Changing Materials (PCMs). *Polymers* **2020**, *12*, 467. [CrossRef] [PubMed]
- 32. Gariboldi, E.; Colombo, L.P.M.; Fagiani, D.; Li, Z. Methods to Characterize Effective Thermal Conductivity, Diffusivity and Thermal Response in Different Classes of Composite Phase Change Materials. *Materials* **2019**, *12*, 2552. [CrossRef] [PubMed]
- Lane, G.A.; Shamsundar, N. Solar Heat Storage: Latent Heat Materials, Vol. I: Background and Scientific Principles. J. Sol. Energy Eng. 1983, 105, 467. [CrossRef]
- Khudhair, A.M.; Farid, M.M. A review on energy conservation in building applications with thermal storage by latent heat using phase change materials. *Energy Convers. Manag.* 2004, 45, 263–275. [CrossRef]
- 35. Raj, V.A.A.; Velraj, R. Review on free cooling of buildings using phase change materials. *Renew. Sustain. Energy Rev.* **2010**, *14*, 2819–2829. [CrossRef]
- Cabeza, L.F.; Castell, A.; Barreneche, C.; De Gracia, A.; Fernández, A.I. Materials used as PCM in thermal energy storage in buildings: A review. *Renew. Sustain. Energy Rev.* 2011, 15, 1675–1695. [CrossRef]
- 37. Dincer, I.; Rosen, M.A. Thermal Energy Storage. Systems and Applications; Wiley: Chichester, UK, 2011.
- 38. Souayfane, F.; Fardoun, F.; Biwole, P.-H. Phase change materials (PCM) for cooling applications in buildings: A review. *Energy Build.* **2016**, *129*, 396–431. [CrossRef]
- 39. Zeinelabdein, R.; Omer, S.; Gan, G. Critical review of latent heat storage systems for free cooling in buildings. *Renew. Sustain. Energy Rev.* **2018**, *82*, 2843–2868. [CrossRef]
- 40. Jaguemont, J.; Omar, N.; Van den Bossche, P.; Mierlo, J. Phase-change materials (PCM) for automotive applications: A review. *Appl. Therm. Eng.* **2018**, 132, 308–320. [CrossRef]
- 41. Grigor'Ev, I.S.; Dedov, A.V.; Eletskii, A.V. Phase Change Materials and Power Engineering. *Therm. Eng.* **2021**, *68*, 257–269. [CrossRef]
- 42. Elias, C.; Stathopoulos, V. A comprehensive review of recent advances in materials aspects of phase change materials in thermal energy storage. *Energy Procedia* **2019**, *161*, 385–394. [CrossRef]
- 43. Eletskii, A.V. Transport properties of carbon nanotubes. Phys. Uspekhi 2009, 52, 209–224. [CrossRef]
- 44. Eletskii, A.V.; Iskandarova, I.M.; Knizhnik, A.A.; Krasikov, D. Graphene: Fabrication methods and thermophysical properties. *Phys. Uspekhi* **2011**, *54*, 227–258. [CrossRef]
- 45. Erlbeck, L.; Schreiner, P.; Schlachter, K.; Dörnhofer, P.; Fasel, F.; Methner, F.-J.; Rädle, M. Adjustment of thermal behavior by changing the shape of PCM inclusions in concrete blocks. *Energy Convers. Manag.* **2018**, *158*, 256–265. [CrossRef]
- 46. Silva, T.; Vicente, R.; Amaral, C.; Figueiredo, A. Thermal performance of a window shutter containing PCM: Numerical validation and experimental analysis. *Appl. Energy* **2016**, *179*, 64–84. [CrossRef]
- Yamamoto, T.; Watanabe, S.; Watanabe, K. Universal Features of Quantized Thermal Conductance of Carbon Nanotubes. *Phys. Rev. Lett.* 2004, 92, 075502. [CrossRef]
- 48. Brown, E.; Hao, L.; Gallop, J.C.; Macfarlane, J.C. Ballistic thermal and electrical conductance measurements on individual multiwall carbon nanotubes. *Appl. Phys. Lett.* **2005**, *87*, 023107. [CrossRef]
- 49. Dresselhaus, M.S.; Dresselhaus, G.; Eklund, P.C. *Science of Fullerenes and Carbon Nanotubes*; Academic Press: San Diego, CA, USA, 1996.
- 50. Saito, R.; Dresselhaus, M.S.; Dresselhaus, G. Physical Properties of Carbon Nanotubes; Imperial Colledge Press: London, UK, 1998.
- 51. Dresselhaus, M.S.; Dresselhaus, G.; Avouris, P. (Eds.) *Carbon Nanotubes: Synthesis, Structure, Properties, and Applications*; Springer: Berlin/Heidelberg, Germany, 2001.
- Ghosh, S.; Calizo, I.; Teweldebrhan, D.; Pokatilov, E.P.; Nika, D.L.; Balandin, A.A.; Bao, W.; Miao, F.; Lau, C.N. Extremely high thermal conductivity of graphene: Prospects for thermal management applications in nanoelectronic circuits. *Appl. Phys. Lett.* 2008, 92, 151911. [CrossRef]
- 53. Balandin, A.A.; Ghosh, S.; Bao, W.; Calizo, I.; Teweldebrhan, D.; Miao, F.; Lau, C.N. Superior Thermal Conductivity of Single-Layer Graphene. *Nano Lett.* 2008, *8*, 902–907. [CrossRef]
- Ghosh, S.; Bao, W.; Nika, D.L.; Subrina, S.; Pokatilov, E.P.; Lau, C.N.; Balandin, A.A. Dimensional crossover of thermal transport in few-layer graphene. *Nat. Mater.* 2010, *9*, 555–558. [CrossRef]
- 55. Abedpour, N.; Neek-Amal, M.; Asgari, R.; Shahbazi, F.; Nafari, N.; Tabar, M.R.R. Roughness of undoped graphene and its short-range induced gauge field. *Phys. Rev. B* 2007, *76*, 195407. [CrossRef]
- 56. Klemens, P.; Pedraza, D. Thermal conductivity of graphite in the basal plane. Carbon 1994, 32, 735–741. [CrossRef]
- 57. Klemens, P.G. The Scattering of Low-Frequency Lattice Waves by Static Imperfections. *Proc. Phys. Soc. Sect. A* **1955**, *68*, 1113–1128. [CrossRef]
- 58. Klemens, P.G. Theory of the A-plane thermal conductivity of graphene. J. Wide Bandgap Mater. 2000, 7, 332. [CrossRef]
- 59. Nika, D.; Pokatilov, E.P.; Askerov, A.S.; Balandin, A. Phonon thermal conduction in graphene: Role of Umklapp and edge roughness scattering. *Phys. Rev. B* 2009, *79*, 155413. [CrossRef]
- Schwamb, T.; Burg, B.R.; Schirmer, N.C.; Poulikakos, D. An electrical method for the measurement of the thermal and electrical conductivity of reduced graphene oxide nanostructures. *Nanotechnology* 2009, 20, 405704. [CrossRef]
- 61. Hummers, W.S., Jr.; Offeman, R.E. Preparation of Graphitic Oxide. J. Am. Chem. Soc. 1958, 80, 1339. [CrossRef]
- 62. Bocharov, G.; Eletskii, A. Percolation Conduction of Carbon Nanocomposites. Int. J. Mol. Sci. 2020, 21, 7634. [CrossRef]

- 63. Bocharov, G.; Eletskii, A.; Mel'Nikov, V. Electrical properties of thermally reduced graphene oxide. *Nanosyst. Phys. Chem. Math.* **2018**, *9*, 98–101. [CrossRef]
- 64. Bocharov, G.S.; Eletskii, A.V. Percolation Transition under Thermal Reduction of Graphene Oxide. *J. Struct. Chem.* **2018**, *59*, 806–814. [CrossRef]
- 65. Nika, D.; Ghosh, S.; Pokatilov, E.P.; Balandin, A. Lattice thermal conductivity of graphene flakes: Comparison with bulk graphite. *Appl. Phys. Lett.* **2009**, *94*, 203103. [CrossRef]
- Knizhnik, A.; Eletskii, A.; Iskandarova, I.; Krasikov, D.; Potapkin, B.; Tilak, V.; Raghavan, K. Molecular dynamics calculation of the thermal conductivity of graphene. In Proceedings of the MRS Conference, Boston, MA, USA, 13–17 April 2009.
- Hu, J.; Ruan, X.; Chen, Y.P. Thermal Conductivity and Thermal Rectification in Graphene Nanoribbons: A Molecular Dynamics Study. Nano Lett. 2009, 9, 2730–2735. [CrossRef] [PubMed]
- 68. Kondo, N.; Yamamoto, T.; Watanabe, K. Molecular-dynamics simulations of thermal transport in carbon nanotubes with structural defects. *e-J. Surf. Sci. Nanotechnol.* **2006**, *4*, 239–243. [CrossRef]
- 69. Bauhofer, W.; Kovacs, J.Z. A review and analysis of electrical percolation in carbon nanotube polymer composites. *Compos. Sci. Technol.* **2009**, *69*, 1486–1498. [CrossRef]
- Aryanfar, A.; Medlej, S.; Tarhini, A.; Damadi, S.R.; Tehrani, A.R.B.; Goddard, W.A., III. 3D percolation modeling for predicting the thermal conductivity of graphene-polymer composites. *Comput. Mater. Sci.* 2021, 197, 110650. [CrossRef]
- Burger, N.; Laachachi, A.; Ferriol, M.; Lutz, M.; Toniazzo, V.; Ruch, D. Review of thermal conductivity in composites: Mechanisms, parameters and theory. *Prog. Polym. Sci.* 2016, *61*, 1–28. [CrossRef]
- 72. Li, A.; Zhang, C.; Zhang, Y.-F. Thermal Conductivity of Graphene-Polymer Composites: Mechanisms, Properties, and Applications. *Polymers* **2017**, *9*, 437. [CrossRef]
- 73. Chen, H.; Ginzburg, V.V.; Yang, J.; Yang, Y.; Liu, W.; Huang, Y.; Du, L.; Chen, B. Thermal conductivity of polymer-based composites: Fundamentals and applications. *Prog. Polym. Sci.* **2016**, *59*, 41–85. [CrossRef]
- 74. Yu, A.; Ramesh, P.; Itkis, M.E.; Bekyarova, E.; Haddon, R.C. Graphite Nanoplatelet–Epoxy Composite Thermal Interface Materials. *J. Phys. Chem. C* 2007, 111, 7565–7569. [CrossRef]
- Irwin, P.C.; Cao, P.; Bansal, A.; Schadler, L.S. Thermal and mechanical properties of polyimide nanocomposites. In Proceedings of the 2003 Annual Report Conference on Electrical Insulation and Dielectric Phenomena, Albuquerque, NM, USA, 19–22 October 2003; pp. 120–123.
- 76. Min, C.; Yu, D.; Cao, J.; Wang, G.; Feng, L. A graphite nanoplatelet/epoxy composite with high dielectric constant and high thermal conductivity. *Carbon* **2013**, *55*, 116–125. [CrossRef]
- 77. Al-Saygh, A.; Ponnamma, D.; Almaadeed, M.A.; Vijayan, P.P.; Karim, A.; Hassan, M.K. Flexible Pressure Sensor Based on PVDF Nanocomposites Containing Reduced Graphene Oxide-Titania Hybrid Nanolayers. *Polymers* **2017**, *9*, 33. [CrossRef] [PubMed]
- Li, Y.; Lian, H.; Hu, Y.; Chang, W.; Cui, X.; Liu, Y. Enhancement in Mechanical and Shape Memory Properties for Liquid Crystalline Polyurethane Strengthened by Graphene Oxide. *Polymers* 2016, *8*, 236. [CrossRef] [PubMed]
- Kim, D.S.; Dhand, V.; Rhee, K.Y.; Park, S.-J. Study on the Effect of Silanization and Improvement in the Tensile Behavior of Graphene-Chitosan-Composite. *Polymers* 2015, 7, 527–551. [CrossRef]
- Kim, H.; Macosko, C.W. Processing-property relationships of polycarbonate/graphene composites. *Polymers* 2009, 50, 3797–3809. [CrossRef]
- Battegazzore, D.; Fadda, E.; Fina, A. Flexible and High Thermal Conductivity Composites Based on Graphite Nanoplates Paper Impregnated with Polydimethylsiloxane. J. Compos. Sci. 2021, 5, 309. [CrossRef]
- 82. Teng, C.C.; Ma, C.C.M.; Lu, C.H.; Yang, S.Y.; Lee, S.H.; Hsiao, M.C.; Yen, M.Y.; Chiou, K.C.; Lee, T.M. Thermal conductivity and structure of non-covalent functionalized graphene/epoxy composites. *Carbon* **2011**, *49*, 5107–5116. [CrossRef]
- Song, S.H.; Park, K.H.; Kim, B.H.; Choi, Y.W.; Jun, G.H.; Lee, D.J.; Kong, B.S.; Paik, K.W.; Jeon, S. Enhanced thermal conductivity of epoxy-graphene composites by using non-oxidized graphene flakes with non-covalent functionalization. *Adv. Mater.* 2013, 25, 732–737. [CrossRef]
- Wang, F.; Drzal, L.T.; Yan, Q.; Huang, Z. Mechanical properties and thermal conductivity of graphene nanoplatelet/epoxy composites. J. Mater. Sci. 2015, 50, 1082–1093. [CrossRef]
- 85. Wan, Y.-J.; Tang, L.-C.; Gong, L.-X.; Yan, D.; Li, Y.-B.; Wu, L.-B.; Jiang, J.-X.; Lai, G.-Q. Grafting of epoxy chains onto graphene oxide for epoxy composites with improved mechanical and thermal properties. *Carbon* **2014**, *69*, 467–480. [CrossRef]
- 86. Qian, R.; Yu, J.; Wu, C.; Zhai, X.; Jiang, P. Alumina-coated graphene sheet hybrids for electrically insulating polymer composites with high thermal conductivity. *RSC Adv.* **2013**, *3*, 17373–17379. [CrossRef]
- Sun, R.; Yao, H.; Zhang, H.-B.; Li, Y.; Mai, Y.-W.; Yu, Z.-Z. Decoration of defect-free graphene nanoplatelets with alumina for thermally conductive and electrically insulating epoxy composites. *Compos. Sci. Technol.* 2016, 137, 16–23. [CrossRef]
- Kim, S.Y.; Noh, Y.J.; Yu, J. Thermal conductivity of graphene nanoplatelets filled composites fabricated by solvent-free processing for the excellent filler dispersion and a theoretical approach for the composites containing the geometrized fillers. *Compos. Part A Appl. Sci. Manuf.* 2015, 69, 219–225. [CrossRef]
- 89. Gu, J.; Xie, C.; Li, H.; Dang, J.; Geng, W.; Zhang, Q. Thermal percolation behavior of graphene nanoplatelets/polyphenylene sulfide thermal conductivity composites. *Polym. Compos.* **2014**, *35*, 1087–1092. [CrossRef]

- Dai, W.; Yu, J.; Liu, Z.; Wang, Y.; Song, Y.; Lyu, J.; Bai, H.; Nishimura, K.; Jiang, N. Enhanced thermal conductivity and retained electrical insulation for polyimide composites with SiC nanowires grown on graphene hybrid fillers. *Compos. Part A Appl. Sci. Manuf.* 2015, 76, 73–81. [CrossRef]
- 91. Tian, L.; Wang, Y.; Li, Z.; Mei, H.; Shang, Y. The thermal conductivity-dependant drag reduction mechanism of water droplets controlled by graphene/silicone rubber composites. *Exp. Therm. Fluid Sci.* **2017**, *85*, 363–369. [CrossRef]
- Chen, J.; Chen, X.; Meng, F.; Li, D.; Tian, X.; Wang, Z.; Zhou, Z. Super-high thermal conductivity of polyamide-6/graphenegraphene oxide composites through in situ polymerization. *High Perform. Polym.* 2017, 29, 585–594. [CrossRef]
- 93. Guo, W.; Chen, G. Fabrication of graphene/epoxy resin composites with much enhanced thermal conductivity via ball milling technique. J. Appl. Polym. Sci. 2014, 131, 338–347. [CrossRef]
- 94. Yu, J.; Qian, R.; Jiang, P. Enhanced thermal conductivity for PVDF composites with a hybrid functionalized graphene sheetnanodiamond filler. *Fibers Polym.* 2013, 14, 1317–1323. [CrossRef]
- Zong, P.; Fu, J.; Chen, L.; Yin, J.; Dong, X.; Yuan, S.; Shi, L.; Deng, W. Effect of aminopropylisobutyl polyhedral oligomeric silsesquioxane functionalized graphene on the thermal conductivity and electrical insulation properties of epoxy composites. *RSC Adv.* 2016, *6*, 10498–10506. [CrossRef]
- Ma, W.-S.; Wu, L.; Yang, F.; Wang, S.-F. Non-covalently modified reduced graphene oxide/polyurethane nanocomposites with good mechanical and thermal properties. J. Mater. Sci. 2014, 49, 562–571. [CrossRef]
- Cho, E.-C.; Huang, J.-H.; Li, C.-P.; Chang-Jian, C.-W.; Lee, K.-C.; Hsiao, Y.-S.; Huang, J.-H. Graphene-based thermoplastic composites and their application for LED thermal management. *Carbon* 2016, 102, 66–73. [CrossRef]
- Wang, Z.; Tong, J.; Li, W.; Zhang, H.; Hu, M.; Chen, H.; He, H. Highly Enhancing Electrical, Thermal, and Mechanical Properties of Polypropylene/Graphite Intercalation Compound Composites by In Situ Expansion during Melt Mixing. *Polymers* 2021, 13, 3095. [CrossRef] [PubMed]
- Varenik, M.; Nadiv, R.; Levy, I.; Vasilyev, G.; Regev, O. Breaking through the Solid/Liquid Processability Barrier: Thermal Conductivity and Rheology in Hybrid Graphene–Graphite Polymer Composites. ACS Appl. Mater. Interfaces 2017, 9, 7556–7564. [CrossRef] [PubMed]
- Chakraborty, A.K.; Plyhm, T.; Barbezat, M.; Necola, A.; Terrasi, G. Carbon nanotube (CNT)–epoxy nanocomposites: A systematic investigation of CNT dispersion. J. Nanopart. Res. 2011, 13, 6493–6506. [CrossRef]
- 101. Tarhini, A.A.; Tehrani-Bagha, A.R. Graphene-based polymer composite films with enhanced mechanical properties and ultra-high in-plane thermal conductivity. *Compos. Sci. Technol.* **2019**, *184*, 107797. [CrossRef]
- 102. Wang, J.; Li, C.; Li, J.; Weng, G.J.; Su, Y. A multiscale study of the filler-size and temperature dependence of the thermal conductivity of graphene-polymer nanocomposites. *Carbon* **2021**, 175, 259–270. [CrossRef]
- 103. Kumar, P.; Yu, S.; Shahzad, F.; Hong, S.M.; Kim, Y.-H.; Koo, C.M. Ultrahigh electrically and thermally conductive self-aligned graphene/polymer composites using large-area reduced graphene oxides. *Carbon* **2016**, *101*, 120–128. [CrossRef]
- Shahil, K.M.F.; Balandin, A.A. Graphene–Multilayer Graphene Nanocomposites as Highly Efficient Thermal Interface Materials. Nano Lett. 2012, 12, 861–867. [CrossRef] [PubMed]
- 105. Ji, C.; Yan, C.; Wang, Y.; Xiong, S.; Zhou, F.; Li, Y.; Sun, R.; Wong, C.-P. Thermal conductivity enhancement of CNT/MoS2/ graphene–epoxy nanocomposites based on structural synergistic effects and interpenetrating network. *Compos. Part B Eng.* 2019, 163, 363–370. [CrossRef]
- 106. Yan, H.; Tang, Y.; Long, W.; Li, Y. Enhanced thermal conductivity in polymer composites with aligned graphene nanosheets. J. Mater. Sci. 2014, 49, 5256–5264. [CrossRef]
- 107. Liu, Z.-P.; Yang, R. Synergistically-Enhanced Thermal Conductivity of Shape-Stabilized Phase Change Materials by Expanded Graphite and Carbon Nanotube. *Appl. Sci.* 2017, 7, 574. [CrossRef]