

The effect of graphene nanoparticles on the thermal conductivity enhancement of organic phase change material and its energy storage properties

PAULINA ROLKA*
MARCIN LACKOWSKI

Institute of Fluid Flow Machinery, Polish Academy of Sciences, Fiszerka
14, 80-231 Gdańsk, Poland

Abstract Organic phase change materials (PCMs), which are typically used as the accumulating material in latent heat thermal energy storage, provide chemical and thermal stability, but have low thermal conductivity. This limits heat transfer rates and prolongs storage charging/discharging time. A method to improve the thermal conductivity of organic PCMs is to add nanomaterials with high thermal conductivity. The paper presents the research on the effect of the addition of graphene nanoparticles (GNPs) on the thermal conductivity of organic PCM (RT28 HC), and its energy storage properties. The transient hot wire and the pipe Poensgen apparatus methods were used to measure thermal conductivity, and the differential scanning calorimetry method was used to determine the heat capacity and phase change temperature. The achieved characteristics of thermal conductivity depending on the amount of added graphene nanoparticles (and stabilizer) indicate that GNPs allow to increase the thermal conductivity on average by 26–87% in the solid state and by 7–28% in the liquid, but this reduces the PCM heat capacity. Therefore, the paper indicates what mass fraction of dopants is optimal to achieve the greatest improvement in thermal conductivity of RT28 HC and its smallest reduction in heat capacity, to use this nano-enhanced PCM in practice.

Keywords: Phase change materials (PCMs); Nano-enhanced phase change materials (NEPCMs); Thermal conductivity; Heat capacity; Latent heat thermal energy storage (LHTES)

*Corresponding Author. Email: prolka@imp.gda.pl

Nomenclature

C	–	heat storage capacity (combination of latent and sensible heat in a specific temperature range), J/g
d	–	diameter, m
I	–	current, A
L	–	pipe length, m
T	–	temperature, K
T_m	–	melting temperature of PCM, K
T_s	–	solidification temperature of PCM, K
U	–	voltage, V

Greek symbols

λ	–	thermal conductivity, W/m·K
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Subscripts

l	–	liquid
p	–	pipe
s	–	solid

Acronyms

DSC	–	differential scanning calorimetry
GNP	–	graphene nanoparticles
MTPS	–	modified transient plane source
MWCNT	–	multi-walled carbon nanotubes
NEPCM	–	nano-enhanced phase change material
LHTES	–	latent heat thermal energy storage
PCM	–	phase change material
PPA	–	pipe Poensgen apparatus
SDBS	–	sodium dodecylbenzenesulfonate
THM	–	T-history method
THW	–	transient hot wire
3LC	–	three-layer calorimeter

1 Introduction

The growing demand for energy and human activities harmful to the environment make it necessary to carry out an energy transformation towards renewable energy sources. Due to the periodic and time-varying availability of renewable energy sources, depending on weather conditions, the use of energy storage facilities is required. Thermal energy generated in renewable energy systems can be stored using the following types of thermal energy storage (TES): sensible heat thermal energy storage (e.g. water

tanks), latent heat thermal energy storage (LHTES) or thermochemical storage. Among them, latent heat thermal energy storage units are increasingly used, which, compared to “cheaper” water tanks, are characterized by a higher energy storage density and ensure the optimal size of the energy storage tank [1], and compared to thermochemical energy storage units, they do not require high temperatures of the processes that determine energy storage and have moderate operational problems [2].

The accumulating material in LHTES units are phase change materials (PCMs) which have the ability to absorb and release energy during a phase transition, usually occurring from a solid to a liquid state (and *vice versa*), in a specific temperature range. LHTES can store heat from solar collector systems [3, 4], waste heat [5], cold from night ventilation systems [6], or energy generated from wind power and photovoltaic installations [4], and next allows to use it to support building’s heating/cooling systems like e.g. HVAC (heating, ventilation, air conditioning), heat pumps or district heating networks [7–10]. Moreover, PCMs can be used separately – encapsulated PCM (usually macroencapsulated PCM) can be incorporated into building elements (e.g. walls, floors, suspended ceilings) and passively improve thermal comfort in rooms [11, 12], or can allow for cooling of photovoltaic panels [13] or electronics [14, 15].

In practice, organic phase change materials are most often used because, compared to inorganic materials, there is no phase separation and they exhibit little or no undercooling, which makes them chemically and thermally stable during many phase change cycles. They also have high latent heat and compatibility with most materials. However, the problem with organic PCMs is their low thermal conductivity that increases the thermal resistance during the phase change process, limits heat transfer and prolongs the time of PCMs melting and solidification, and thus impacts charging/discharging time of the thermal storage. This can result in ineffective use of accumulation materials in the case of sources with a relatively short lifespan (e.g. waste heat from technological processes, solar energy), and a reduction of effectiveness and cost-effectiveness of the LHTES application.

To avoid too long charging/discharging times of storages with PCMs, the heat transfer surface in LHTES is increased or methods are proposed to increase the thermal conductivity of storage materials. Increasing the area of heat exchange in LHTES can be achieved by using special fins in the construction of storages (e.g. longitudinal, radial, ring, round), using fin-and-tube heat exchangers, or using capillary tube bundles as heat exchangers,

also using encapsulated PCM (macro- or micro-encapsulated) [7, 16, 17]. One of the methods aimed at improving thermal conductivity in LHTES is the use of porous materials (in the form of foams or matrixes) filled with PCM [17, 18]. Although the use of special heat exchangers increasing the heat exchange surface or the use of porous materials improving the intensification of heat transfer shortens the melting/solidification times of PCM, it leads to a significant reduction in the amount of PCM in the tank. As indicated in the analysis [17], the volume of PCM in the total volume of the tank is 30–50% in the case of storage with macro-encapsulated PCM (depending on the type of capsules and packaging), 35–90% in the case of storage with fins and a fin-tube exchanger, 60–90% in the case of storage with a porous structure, over 90% in the case of storage with a capillary bundle as a heat exchanger. Therefore, these solutions may lead to a reduction in heat capacity or an increase in the mass and volume of the storage tank, and thus generate a higher cost per unit of stored energy.

Another way to reduce the charging and discharging times of LHTES is to directly improve the thermal conductivity of organic phase change materials by adding admixtures in the form of nanomaterials with high thermal conductivity [19, 20]. Nanomaterials added to organic PCMs may be metal nanoparticles, metal oxide nanoparticles or carbon-based nanoparticles [19–21]. Wu *et al.* [21] indicate that after adding copper nanoparticles to paraffin (at a content of 2% wt. Cu) achieved a maximum increase in thermal conductivity up to 14.2% in the solid state and 18.1% in the liquid. Temel *et al.* [22] investigated the effect of various nanoparticles (metal oxide nanoparticles and carbon nanoparticles) on improving the thermal conductivity of organic PCM – a commercially available material called A82. The results of their research indicate that the improvement in thermal conductivity of A82 composites doped with a 5% mass fraction of metal oxide nanoparticles: ZnO, TiO₂, Al₂O₃ and MgO was 2.6%, 3.6%, 6.5% and 8.4%, respectively. A higher improvement in thermal conductivity was achieved using carbon nanoparticles – multi-walled carbon nanotubes (MWCNT) and graphene nanoparticles (GNP), obtaining an increase of 26.7% and 154.9%, respectively. Moreover, their research indicates that by adding admixtures, the latent heat of the base PCM is reduced by up to 18%, depending on the type of nanoparticles and their mass fraction. Only when zinc oxide nanoparticles were used, the latent heat increased, which the authors of [22] explain as the effect of intermolecular attraction between the nanoparticles and the organic PCM.

A higher thermal conductivity of base organic PCMs as a result of doping them with carbon-based nanoparticles rather than with metal oxide nanoparticles was reported in the works [15,19,20,23]. The research of Radhakrishnan *et al.* [23] indicates that after adding nanomaterials with a mass content of 0.1% and 1%, an increase in thermal conductivity was achieved by approx. 7% and 17% for Al₂O₃ nanoparticles, 7% and 18% for SiO₂ nanoparticles, 12% and 30% for graphene nanoparticles. They also noted a decrease in latent heat of approx. 7% and 27% for Al₂O₃ nanoparticles, 7% and 14% for SiO₂ nanoparticles, 7% and 21% for graphene nanoparticles. Moreover, this investigation showed that after some time, nanoparticles and PCM may separate in the liquid – sedimentation of nanomaterials occurs. The sedimentation of nanoparticles in nano-enhanced PCMs (NEPCMs) is noted in the works [19, 20, 24]. To improve the stability of NEPCMs, the use of surfactants is proposed [15,19,20,24]. Choi *et al.* [24] conducted tests, in which they showed that adding a surfactant in the form of polyvinylpyrrolidone (PVP) stabilizes NEPCM in the liquid state even for several days. Studies have shown that the thermal conductivity of NEPCM (stearic acid with graphene nanoparticles, or graphite nanoparticles or MWCNT nanoparticles) without added surfactant has a lower value than for NEPCM with a stabilizer (polyvinylpyrrolidone). Moreover, the highest improvement in thermal conductivity was achieved when graphene nanoparticles were added to organic PCM (stearic acid).

The paper presents research on improving the thermal conductivity of the organic phase change material, namely RT28 HC (with a melting point in the range of 27–29°C), which could be used in LHTES integrated with heating and cooling installations of buildings, as well as for cooling photovoltaic panels or microelectronics. Based on the literature analysis, it was decided to improve the thermal conductivity of the RT28 HC material by adding graphene nanoparticles with a mass fraction in the range of 1–5% and a surfactant to ensure stability. Although tests on improving the thermal conductivity of RT28 HC as a result of adding graphene, MWCNT, Al₂O₃, or CuO nanoparticles to it were already carried out in [15], they were only carried out for a 1% mass fraction of nanoparticles. Therefore, the aim of the research presented in the article is to present the characteristics of the influence of graphene nanoparticles on the thermal conductivity and latent heat of the base RT28 HC (organic PCM) depending on the weight fraction of the nanoparticles, which has not been carried out so far. The experimental results of thermal conductivity tests presented in the manuscript were carried out using two different measurement methods

other than that used in [15]. The first one is the transient hot wire method (usually used in the measurement of NEPCMs) and the second is the pipe Poensgen apparatus method, which has not been used so far to measure the thermal conductivity of NEPCMs. The comparison of thermal conductivity values achieved by different thermal conductivity measurement methods aims to clearly determine the increase in thermal conductivity as a result of the use of nanoadditives – graphene nanoparticles and surfactant (nanoparticle stabilizer). Moreover, the work also considers the influence of different weight contents of nanoparticles on other thermophysical properties of the base PCM, e.g. the temperature range of the phase change of the tested material. Additionally, the presented results of experimental work provide valuable knowledge about what mass fraction of graphene nanoparticles is the optimum, between achieving the greatest improvement of the thermal conductivity of the organic PCM and the lowest possible reduction in its heat capacity, which has a significant impact on the application of NEPCM in practice.

2 Materials and methods

2.1 Materials used and preparation of nano-enhanced phase change material

The organic phase change material, that was the subject of the research on increasing its thermal conductivity in the presented article, was a commercially available material, namely RT28 HC (Rubitherm GmbH). The RT28 HC material was selected for testing due to the wide range of possible applications of stored energy in practice (e.g. refrigeration installations, heating installations, passive cooling in suspended ceilings, cooling of photovoltaic (PV) modules and microelectronics), as well as due to its well-known thermophysical properties, which are presented in Table 1.

Graphene nanoparticles (GNP), were chosen as the material to help increase the thermal conductivity of the base PCM (RT28 HC) because they are characterized by high thermal conductivity (from 3000 W/m·K to 5000 W/m·K) [25], and compared to other used nanomaterials in previous studies [15, 22–24] showed the greatest improvement in thermal conductivity of phase change materials. In this research, commercially available GNPs are used with the following properties: particle size up to $2 \cdot 10^{-6}$ m, thickness $(1-4) \cdot 10^{-9}$ m, specific surface area 700–800 m²/g and purity 91%, specified by the manufacturer (PlasmaChem GmbH [26]). In the litera-

Table 1: Thermophysical properties of base organic PCM – RT28 HC (a summary of data from the literature [6, 15, 28–30]).

Properties	Method							
	3LC	THM	THM	DSC			PPA	MTPS
				Heating rate				
				1 K/min	1 K/min	2 K/min		
T_m (K)	301.15	300.46	–	302.04	307.00	302.03	–	–
T_s (K)	300.15	300.79	–	299.95	300.65	300.18	–	–
C (J/g)*	250	268 ^h 220 ^c 244 ^{av}	246	255 ^h 258 ^c 256.5 ^{av}	258 ^h 252 ^c 255 ^{av}	250	–	–
λ_s (W/m·K)	–	–	–	–	–	–	0.33	0.22
λ_l (W/m·K)	–	–	–	–	–	–	0.20	0.15
Reference	[28]	[6]	[30]	[15]	[29]	[30]	[6]	[15]

^h heating process, ^c cooling process, ^{av} average, * combination (sum) of latent heat and sensible heat at temperature range (294.15–309.15 K).

ture [15, 19, 20, 24], a surfactant – a sodium dodecylbenzenesulfonate (SDBS, manufacturer Sigma-Aldrich [27]) was used to ensure the stability of suspension, after the addition of GNP to the base organic PCM (RT28 HC).

Samples with nano-enhanced PCM (NEPCM) were prepared using a two-step method, in which “ready-made” admixtures (nanomaterials) are added to the base PCM in the liquid, and then the mixture is mixed appropriately [15, 19, 20]. Therefore, the preparation of NEPCM samples started by melting RT28 HC. The RT28 HC material was heated to above 305.15 K and then maintained at approximately 305.15–308.15 K by placing the beaker with liquid PCM on the heating platform of a magnetic stirrer (magnetic stirrer SBS-MR-1600/1T Pro Steinberg). Then, a stabilizer – sodium dodecylbenzenesulfonate was added to the melted PCM in a ratio of 4:1 of graphene nanoparticles (as in [15]) and mixed using a magnetic stirrer at a stirring rate of 450 rpm for 30 min. After that, GNPs with a mass fraction of 1%, 3% and 5% were added to the mixture, respectively, and were stirred by a magnetic stirrer (at 450 rpm) for 2.5 hours. Each obtained solution was poured from the beaker into a special vessel and then mixed using an ultrasonic mixer (Sonoplus HD 2070.2 Bandelin) for 1 hour to achieve uniform and intense sonication (dispersion of nanoparticles in NEPCM). As a result, samples with three NEPCMs differing in the mass fraction of nanomaterials (nanoparticles of GNP and SDBS) were obtained.

2.2 Methods of measuring the thermal conductivity of base phase change material and nano-enhanced phase change material

Two different methods were used to measure the thermal conductivity of the base PCM (RT28 HC) and NEPCM: the transient hot wire (THW) method and the pipe Poensgen apparatus (PPA) method.

The transient hot wire method is based on placing a linear heat source (heating wire) in the tested material and measuring the temperature increase over time at a specific distance from the heat source. It is assumed that the heat source is powered by electricity and the heat flux released over time is constant and uniform over the entire length of the tested material. The THW method was used in this investigation because this method was the most frequently used in other research of NEPCM [19, 20]. Measurements using the THW method were carried out using a commercial device – a thermal properties analyzer TEMPOS (METER Group) along with two measurement sensors: KS-3 and SH-3 (see Fig. 1). The SH-3 measurement probe was used to measure the thermal conductivity of base PCM and NEPCM in the solid state, and the KS-3 sensor in the liquid.



Figure 1: A commercial device used in the research to measure the thermal conductivity of base PCM and NEPCM using the transient hot wire method.

In the research presented in this paper, the pipe Poensgen apparatus method was used as a second method for measuring the thermal conductivity of the base PCM and NEPCM due to its simple measurement and the ability to perform measurements using a “low cost” device compared to commercial devices typically used in the literature [15, 19–22, 24].

The pipe Poensgen apparatus method is based on the measurement of a ‘steady-state’ temperature difference on walls of two pipes placed concentrically (the outer wall of the inner pipe and the inner wall of the outer pipe), during a constant heat flow from the heat source – an electric heater. During the measurement, the tested material (in this case base PCM or NEPCM) is between the two pipes placed concentrically (see Fig. 2a). Knowing the set heat flux (through the voltage and current setting of the electric heater), and the geometric parameters of the device, the thermal conductivity is determined according to the following relationship

$$\lambda = \frac{UI \ln \frac{d_{p,out}}{d_{p,in}}}{2\pi L (T_{p,in} - T_{p,out})},$$

where $d_{p,in}$, $d_{p,out}$ denote the diameters of the inner and outer pipes, $T_{p,in}$, $T_{p,out}$ – the temperature of the outer wall of the inner pipe and the inner wall of the outer pipe, respectively.

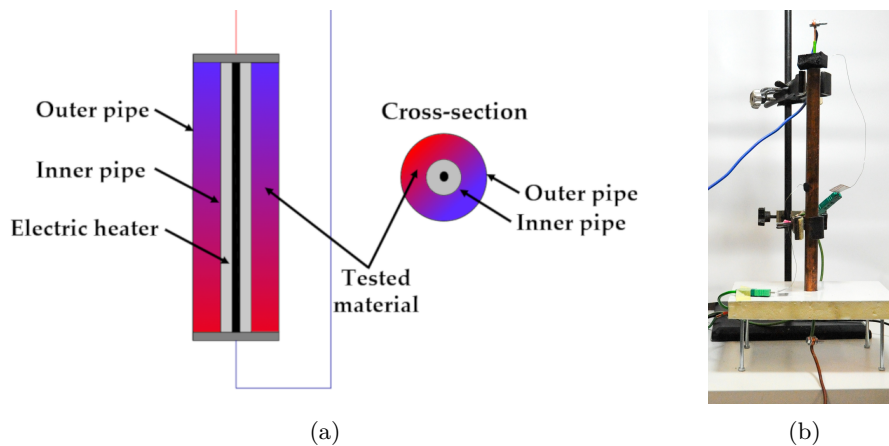


Figure 2: An in-house device for measuring the thermal conductivity of base PCM and NEPCM using the pipe Poensgen apparatus method: (a) simplified conceptual diagram (scheme) of the device’s construction; (b) ready-made device.

The device used in this research, based on the pipe Poensgen apparatus method, for measuring the thermal conductivity of the base PCM and NEPCM, is shown in Fig. 2b, and the technical details regarding to the construction of this device are presented in [4].

2.3 Methods of measuring heat capacity and temperature range of phase change of base phase change material and nano-enhanced phase change material

To investigate the heat capacity and temperature range of phase transition of the base PCM and NEPCM, it was decided to use the differential scanning calorimetry (DSC) method. For this purpose, a commercial measuring device was used, DSC Q2000 (TA Instrument). DSC measurements for samples with base PCM and NEPCM were performed at a constant heating/cooling rate of 1 K/min due to ensuring an optimal measurement time and achieving good agreement of the measurement results compared with the results from other methods (3LC and T-history) in the case of measuring base PCM [6]. Sample tests were carried out in the temperature range 291.15–311.15 K. The samples of the tested materials had masses ranging from approx. $(18\text{--}30)\cdot 10^{-3}$ kg. Samples of the tested NEPCM materials immediately after preparation in the liquid state, were placed in aluminium crucibles with a lid and hermetically closed.

3 Results

Each sample of the tested material, immediately after preparation, in the liquid state was poured into the pipe Poensgen apparatus in an amount of $46 \cdot 10^{-3}$ l. First, measurements were made in the liquid by supplying a heat flow and heating the material to 308.15–310.15 K until a constant temperature gradient of walls in the pipe Poensgen apparatus was achieved. The measurement of the temperature difference at the walls of the device while the tested material was in the liquid lasted several minutes, and on its basis, the thermal conductivity was determined, for which the average value was estimated and marked in grey in Fig. 3a (depending on the mass fraction of GNP in NEPCM). After performing measurements in the liquid, the tested material was left in the pipe Poensgen apparatus to solidify at an ambient temperature of approx. 289.15–290.15 K. The laboratory room was air-conditioned, which allowed the ambient temperature to be set at

approx. 289.15–290.15 K. After complete solidification of the tested material, measurements were made in the solid state. The electric heater (inside the pipe Poensgen apparatus) was set to heat the solidified tested material to the temperature of approx. 294.15 K. After achieving a constant temperature gradient at the walls of the pipe Poensgen apparatus, measurements of the tested material in the solid state began. The obtained averaged thermal conductivity results are shown in grey in Fig. 3b (depending on the mass content of GNP in NEPCM).

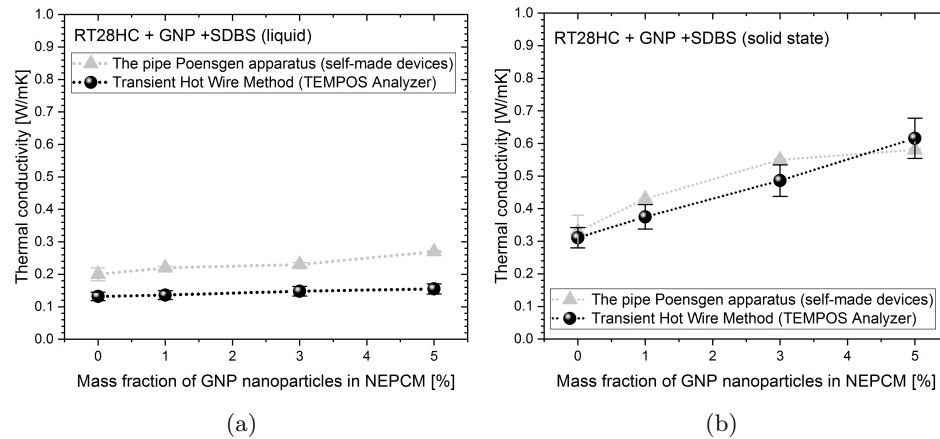


Figure 3: Results of thermal conductivity of NEPCM – RT28 HC with GNP and SDBS admixtures (depending on the content of GNP nanoparticles in the mixture): (a) in the liquid; (b) in the solid state. The thermal conductivity of base RT28 HC (without nanomaterials) was marked by a point of 0% mass fraction.

Right after preparation, material samples (prepared with the same mass fraction of GNP and SDBS nanoparticles as the samples tested in the pipe Poensgen apparatus) were poured into special containers or test tubes with a flat bottom before measurement using the Tempos analyzer. Material samples poured into screw-on test tubes with a flat bottom (after inserting the KS-3 sensor through the hole in the test tube cap) were placed in a thermal chamber filled with air at a temperature of approx. 305.15–306.15 K to perform the measurement in the liquid. The measurement in the liquid was started after the sample temperature stabilized. The measurement in the liquid using the Tempos analyzer was performed 5 times, and the average of the measurements is marked in black in Fig. 3a. These material samples poured into special containers were placed in the refrigerator to “quickly”

solidify, and after solidification, two holes were made in them to place the SH-3 sensor. Thermal conductivity tests in the solid state were carried out at room temperature (approx. 296.15–297.15 K). The solid-state measurement using the Tempos analyzer was performed 5 times, and the results of the average thermal conductivity are marked in black in Fig. 3b.

The results of thermal conductivity measured with the pipe Poensgen apparatus and Tempos analyzer indicate that as the mass fraction of graphene and SDBS in NEPCM increases, the thermal conductivity of organic PCM – RT28 HC increases too (see Fig. 3).

The analysis of measurements of the thermal conductivity of the RT28 HC material in the solid state indicates that depending on the mass content of graphene nanoparticles in the range of 1–5%, the thermal conductivity increases by 0.1–0.25 W/m·K when measured using the pipe Poensgen apparatus, and by 0.06–0.30 W/m·K when measured with the Tempos analyzer (see Fig. 3b), compared to the thermal conductivity of “pure” RT28 HC. The highest thermal conductivity in the solid state was obtained by RT28 HC with SDBS and 5% GNP mass fraction, the value of which when measured with the pipe Poensgen apparatus was 0.58 ± 0.03 W/m·K, and measured with a Tempos analyzer was 0.62 ± 0.06 W/m·K. On the other hand, the thermal conductivity of RT28 HC with SDBS and 1% GNP mass fraction reached 0.43 ± 0.001 W/m·K with the pipe Poesngen apparatus, and 0.38 ± 0.04 W/m·K with the Tempos analyzer.

The results of thermal conductivity in the liquid indicate an increase in the thermal conductivity of RT28 HC as a result of doping it with GNP and SDBS (depending on the mass fraction of GNP in the range of 1–5%) by 0.02–0.07 W/m·K in measurements with the pipe Poensgen apparatus, and by 0.004–0.023 W/m·K in measurements with the Tempos analyzer (see Fig. 3a). The highest thermal conductivity in the liquid was achieved for RT28 HC with SDBS and 5% mass fraction of GNP (0.27 ± 0.002 W/m·K with PPA and approx. 0.16 ± 0.02 W/m·K with the Tempos analyzer), and the lowest for RT28 HC with SDBS and 1% mass fraction of GNP (0.22 ± 0.004 W/m·K with PPA and approx. 0.14 ± 0.01 W/m·K with the Tempos analyzer).

The results of thermal conductivity measurements of the base PCM and prepared NEPCMs obtained using two different measurement methods (PPA and THW methods) reach slightly different values. Slightly higher values are observed for measurements obtained using the pipe Poensgen apparatus method, but it shows very good agreement with the results achieved using the THW method in both states (liquid and solid state).

In order to determine the effect of admixtures (GNP and SDBS nanoparticles) on the properties determining the ability to store energy by organic RT28 HC, such as the heat capacity and the phase change temperature range, NEPCMs with different mass fractions of nanoadditives were tested using the DSC method. A summary of the obtained values of heat capacity and solidification and melting temperatures in DSC measurements is presented in Table 2. However, to clearly show the impact of admixtures on the change in the heat capacity of the base organic PCM, Fig. 4 presents the results of the heat capacity values, determined for the temperature range of 294.15–308.15 K, depending on the mass fraction of GNPs.

Table 2: Thermophysical properties of the base RT28 HC and RT28HC doped with GNP and SDBS obtained in DSC measurement.

Test material	$T_{m,onset}$ (K)	$T_{m,peak}$ (K)	C^h (J/g)	$T_{s,onset}$ (K)	$T_{s,peak}$ (K)	C^c (J/g)
RT28 HC	299.53	302.1	255	299.17	298.15	210
RT28 HC with 1% GNP + SDBS	299.45	302.7	212	299.15	297.44	195
RT28 HC with 3% GNP + SDBS	299.38	301.48	200	299.15	298.29	174
RT28 HC with 5% GNP + SDBS	299.55	301.1	169	299.15	298.93	147

^h heating process, ^c cooling process.

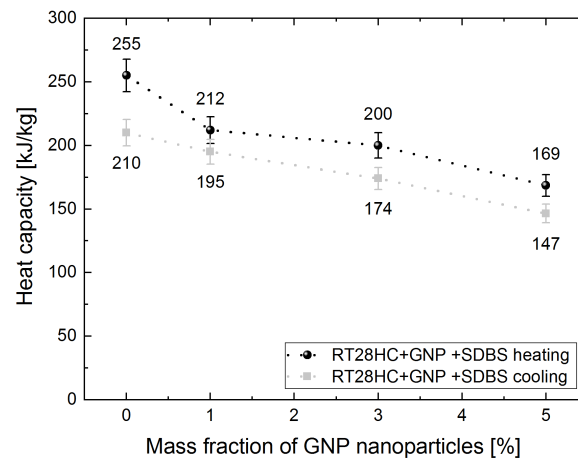


Figure 4: Heat storage capacity results of NEPCM – RT28 HC with GNP and SDBS admixtures (depending on the mass fraction of GNP nanoparticles in the mixture). The heat capacity of base RT28 HC (without nanomaterials) was marked by a point of 0% mass fraction.

The heat capacity results presented in Fig. 4 and Table 2 indicate that as the mass content of admixtures increases, the heat capacity of the base RT28 HC decreases. The decrease in heat capacity in the heating process is 17–34%, and in the cooling process 7–30%. The smallest decrease in heat capacity was obtained for RT28 HC with SDBS and 1% wt. graphene nanoparticles. Based on the DSC measurement results, it was not found that the selected admixtures had an impact on the phase transition temperature range of RT28 HC.

4 Discussion

The thermal conductivity experiment results clearly show that after adding graphene nanoparticles and stabilizer (SDBS) to organic RT28 HC, its thermal conductivity is improved. To determine the effect of graphene nanoparticles and their mass fraction on the improvement of the thermal conductivity of RT28 HC, the thermal conductivity enhancement factor was calculated as the ratio of the thermal conductivity of RT28 HC with the specific mass fraction of GNP to the thermal conductivity of the base RT28 HC (see Fig. 5).

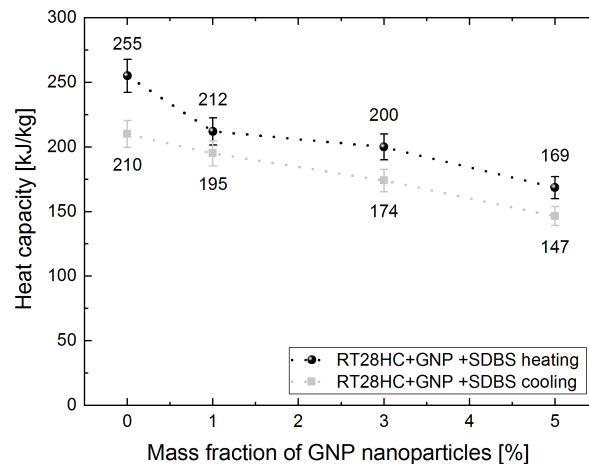


Figure 5: Thermal conductivity enhancement factor of RT28HC with SDBS and GNP nanoparticles (depending on the mass fraction of GNP nanoparticles in NEPCM). The thermal conductivity enhancement factor of base RT28 HC (without nanomaterials) was marked by a point of 0% mass fraction (point 0 – abscissa, and point 1 ordinate).

Based on the thermal conductivity enhancement factor, it can be assumed that the addition of graphene nanoparticles with a weight fraction of 1–5% allowed for an improvement in the thermal conductivity of organic PCM (RT28 HC) by an average of 26–87% in the solid state, and by 7–28% in the liquid. Moreover, a better improvement in thermal conductivity was achieved in the solid state than in the liquid, which was also noticed in the works [15,20]. Because NEPCM has an ordered microstructure in the solid state but not in the liquid, heat is transferred more efficiently in the solid state. On the other hand, adding admixtures to RT28 HC causes a reduction in the heat capacity of “pure” PCM. This happens because the PCM content in the mixture decreases.

Figure 6 shows a comparison of thermal conductivity (average of the results of experimental measurements obtained by the PPA and THW methods) and heat capacity (average of the results of the heating and cooling process obtained by the DSC method) of base organic PCM (RT28 HC) and NEPCM (RT28 HC with GNP and SDBS). Based on Fig. 6, it can be concluded that as the mass fraction of graphene nanoparticles in RT28 HC increases, its thermal conductivity increases and the ability to accumulate energy decreases. In the case of a heating (or cooling) system, where it

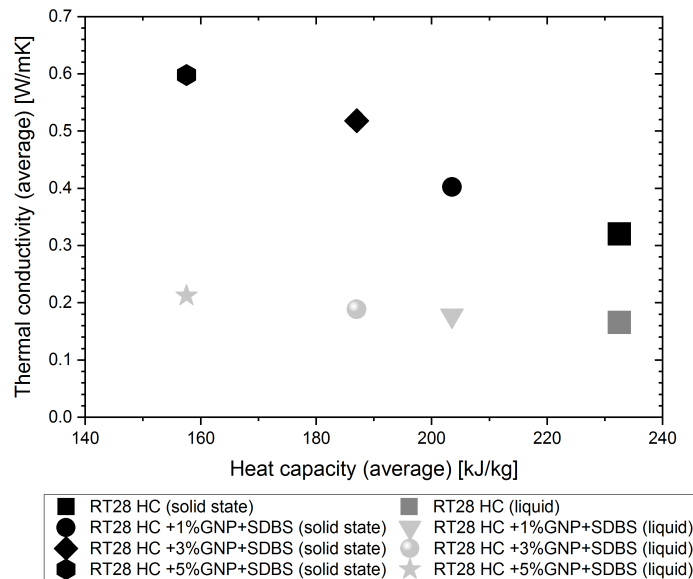


Figure 6: Comparison of thermal conductivity and latent heat obtained in tests of base RT28 HC and RT28 HC with graphene and SDBS nanoparticles.

is required to quickly absorb and release energy by the storage (LHTES), a better choice is to use a phase change material with the highest possible thermal conductivity coefficient, i.e. in this case the highest mass fraction of graphene nanoparticles – RT28 HC with SDBS and 5% weight fraction of graphene nanoparticles. However, in most cases, the decisive factor in choosing the accumulation material for LHTES is its high heat capacity. Therefore, it is important for NEPCM – in this case, RT28 HC with GNP and SDBS, to find the optimum between the increased thermal conductivity and the smallest reduction in the heat capacity of the material. Figure 6 shows that such optimal values are obtained by adding graphene nanoparticles with a mass fraction of 1% to RT28 HC.

5 Conclusions

In this research, the effect of addition of graphene nanoparticles on the thermal conductivity of organic PCM (RT28 HC) and its energy storage properties was investigated. Two independent methods were used to test the thermal conductivity: the transient hot wire method (commonly used in NEPCM measurements) and the pipe Poensgen apparatus method (which has not been used so far to measure the thermal conductivity of NEPCM). Additionally, the DSC method was used to determine the heat capacity and phase change temperature. The results of this research are summarized and the main conclusions are presented as follows:

- thermal conductivity results obtained using the pipe Poensgen apparatus are in good agreement with the measurement results performed using the transient hot wire method (Tempos analyzer);
- the addition of graphene nanoparticles to organic PCM (RT28 HC) increases its thermal conductivity in solids and liquids, and with the increase in the mass fraction of graphene nanoparticles, the enhancement of the thermal conductivity of RT28 HC is greater;
- characteristics of the thermal conductivity enhancement factor show that the addition of graphene nanoparticles (with a weight fraction of 1–5%) allowed for an improvement in the thermal conductivity of RT28 HC by an average of 26–87% in the solid state and by 7–28% in the liquid;

- the addition of graphene nanoparticles and stabilizer (SDBS) does not affect the temperature range of phase change, but reduces the heat capacity of RT28 HC by 17–34% in the heating process and by 7–30% in the cooling process;
- the heat capacity is one of the most important criteria for selecting the storage material in LHTES, so it is important to find the optimum between the increased thermal conductivity coefficient and the smallest reduction in the heat capacity of the material caused by the addition of GNP and SDBS nano-particles to organic PCM;
- characteristic of thermal conductivity versus heat capacity present that the optimal point between the increased thermal conductivity and the reduction in heat capacity is reached for 1% mass fraction of GNP added together with SDBS to RT28 HC.

The research results presented in the article, clearly indicate that the use of graphene nanoparticles has a significant impact on the direct improvement of the thermal conductivity of organic PCM and thus can improve the thermal response of the LHTES storage. Therefore, in the future, it is proposed to carry out comparative tests of the loading and unloading time of LHTES, where the accumulation material will be “pure” RT28 HC and RT28 HC with the addition of SDBS and GNP (with a mass fraction 1%).

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