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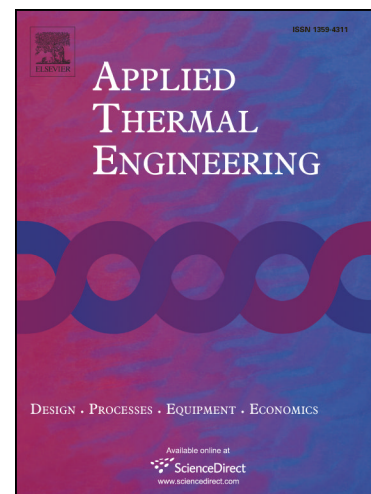
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PII: S1359-4311(19)30317-5
DOI: <https://doi.org/10.1016/j.applthermaleng.2019.113868>
Article Number: 113868
Reference: ATE 113868

To appear in: *Applied Thermal Engineering*

Received Date: 18 January 2019
Revised Date: 24 May 2019
Accepted Date: 27 May 2019



Please cite this article as: D. Cabaleiro, F. Agresti, S. Barison, M.A. Marcos, J.I. Prado, S. Rossi, S. Bobbo, L. Fedele, Development of paraffinic phase change material nanoemulsions for thermal energy storage and transport in low-temperature applications, *Applied Thermal Engineering* (2019), doi: <https://doi.org/10.1016/j.applthermaleng.2019.113868>

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Development of paraffinic phase change material nanoemulsions for thermal energy storage and transport in low-temperature applications

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Abstract

In this study, new phase change material nanoemulsions (PCMEs) were designed and characterized as possible storage and heat transfer media for low-temperature thermal uses. Water- and (ethylene glycol+water)-based emulsions with fine droplets of *n*-heptadecane and RT21HC commercial paraffin were produced by a solvent-assisted emulsification method. No phase separation or significant growth in PCM drops were observed for the prepared emulsions through storage, after freeze-thaw cycles and under mechanical shear. Phase change transitions were characterized and a significant sub-cooling was observed, with solidification temperatures up to 13 K below the melting point. One pure alkane and two commercial paraffin waxes with higher melting points were considered as nucleating agents to reduce sub-cooling effect. Although the emulsions exhibited diminutions in thermal conductivity up to 9% with respect to the carrier fluids used as base fluid, enhancements in energy storage capacity (considering an operational temperature interval equal to the sub-cooling) reached 26% in the case of RT21HC nanoemulsion based on the (ethylene glycol+water) mixture that contained 10% in mass of paraffin. In addition, the thermal reliability of the nanoemulsions was verified analyzing the changes in latent heat after storage and throughout 1000 thermal cycles.

Keywords: thermal energy storage, paraffin, phase change material nanoemulsion (PCME), latent heat, thermal conductivity, density.

1. Introduction

Worldwide concern with environmental and other energy-related issues has prompted an increasing interest in a more efficient use of thermal installations. In this sense, thermal energy storage (TES) is expected to play an important role. Thus, an efficient way to maximize the performance of thermal facilities and correct unbalances between the energy supply and demand is to store energy when available in excess or at low cost, to use it later during scarce periods [1,2]. TES systems utilizing latent heat storage materials, also known as phase change materials (PCMs), are especially attractive since they allow large energy storage densities within reduced temperature intervals [3,4]. Nevertheless, most organic PCMs usually exhibit low thermal conductivity, which leads to low heat transfer rates within the phase change material and prolongs the charging and discharging processes [5].

Several techniques have been investigated to enhance the heat exchanging performance of PCM-systems, such as extending the heat transfer surface or dispersing highly conductive particles [6–9]. Although effective, these options require of additional materials, which sometimes increase the manufacturing cost and reduce the compactness factor of TES systems [10]. An alternative to integrate PCMs in thermal facilities is to use phase changing slurries (PCSs). PCSs are two-phase fluids formulated as a combination of a carrier fluid (continuous phase) with good transport properties and a PCM (dispersed phase) with high latent heat [11]. In these systems, PCM and heat transfer fluid (HTF) can directly exchange thermal energy with large surface-to-volume ratios, which ensure good heat transfer rates of stored energy [5,12]. In addition, as PCM slurries stay pumpable during the phase change, they can be used not only as energy storage materials but also as heat transfer media.

Ice-liquid water mixtures, clathrate hydrate slurries, and macroencapsulated PCM suspensions are common PCSs [11]. However, sedimentation or buoyancy forces of PCM droplets can induce non-homogeneities in the flow state and, consequently, cause problems such as sudden increase in pressure drop or flow blockage [13,14]. Non-homogeneous flow state conditions can be prevented by using microencapsulated PCMs with very small diameters. However, encapsulations increase the manufacturing cost and introduce an additional thermal resistance between PCM and carrier fluid [13]. Another option under extensive research is to utilize phase change material emulsions (PCMEs). In this case, PCM droplets are not coated with a polymer or a thin metallic layer, but stably dispersed in the carrier fluid by the action of appropriate surfactants [15,16]. As shell material and polymerization/coating stage are omitted, size reduction is technically simplified and PCMEs can be synthesized in a more cost-effective manner [12].

Phase change materials must be suitably selected so that the PCM–carrier fluid combination must be immiscible and the phase change transition of the resulting PCM droplets fits in the desired operating temperature range. In the case of aqueous PCMEs, paraffins (straight–chained alkanes) are affordable and fulfill these requirements as they are hydrophobic and exhibit melting points covering a wide temperature interval [15,17]. Small emulsion droplets are desirable to obtain long–term stabilities and moderate rises in pumping power. Since nanoemulsion formation is thermodynamically unfavorable, an appropriate selection of the surfactant and formulation conditions are key issues to prepare fine PCMEs. Several ionic and non–ionic surfactants have been used to produce nanoemulsions using different emulsification methods [15,18,19]. In particular, anionic sodium dodecyl sulfate (SDS) has proven effective in the preparation of paraffin nanoemulsions by ultrasonic processing [15,20].

PCM emulsions with nano–size droplets tend to exhibit sub–cooling (*i.e.* droplets need to be cooled below their melting point so that freezing process begins). This phenomenon is undesirable since stored energy is released at a lower temperature or in a wider temperature range, which thereby may limit or dissuade PCMEs use. Huang et al. [21] experimentally studied the phase change transition of different paraffin–in–water emulsions and found that sub–cooling effect increases up to 15 K with reducing droplet size. Günther et al. [22] attributed this behavior to the deactivation of heterogeneous nucleation as a consequence of size reduction. Thus, in small isolated PCM droplets, phase change is mainly triggered by homogeneous nucleation processes, which usually occur at considerably lower temperatures. A possibility to face this issue is to introduce additional heterogeneous sites in the disperse phase. Nucleating agents (NAs) are substances with a low phase tension that act as nucleus surfaces to start nucleation inside the PCM droplets. Metallic oxide nanoparticles, carbon nanostructures and PCMs with higher melting points than the material in solidification have been previously considered in literature as NAs for PCM nanoemulsions or microencapsulated PCM slurries [18,21,23,24]. However, the nucleating agent does not undergo the phase change and, consequently, the amount of used NA must be limited as much as possible in order to avoid considerably reductions in the store capacity of PCM nanoemulsions [25].

Bulk paraffinic materials like *n*–heptadecane or RT21HC exhibit melting transitions within the range usually accepted for comfort in buildings of most countries [26,27] and have been categorized as potential PCMs for cooling applications such as heating, ventilation and air conditioning (HVAC) [28,29]. Thus, Anisur et al. [30] evaluated the use of bulk *n*–heptadecane as latent heat storage media in a shell and tube exchanger for active cooling of air, while RT21HC was used by Vanaga et al. [31] to design a solar facade module capable, for example, of reducing heating and cooling loads in buildings. Regarding paraffinic PCMEs, previous investigations showed the great

potential of these materials as both energy storage and heat transfer media for a wide range of utilizations such as HVAC systems, cooling circuits of electronic machinery or solar thermal facilities [18,32,33]. However, as recently pointed by Vasile et al. [34], due to practical limitations of PCM emulsions such as instability issues during solidification process, only a limited number of works [16,35–39] have focused on cooling applications such as air conditioned systems. Thus, some key issues must still be addressed in order to let these materials gaining competitive edge over conventional carrier fluids [32]. In this sense, more stability analyses under storage or different operation conditions as well as further research on melting and solidification processes of PCMEs are necessary to fully understand their thermal behavior during phase change.

On the other side, we would also like to call attention on the fact that most works in available literature focused on the formulation of water-based samples. However, aqueous solutions containing glycol are usually preferred as carrier fluids in applications working at temperatures close to the freezing point of water [40]. Up to our knowledge, only Lu et al. [41] considered the addition of glycol to the continuous phase as antifreeze. In that study, authors designed and characterized RT6 emulsions based on a propylene glycol–water mixture 40%:60% and containing paraffin concentrations up to 40 wt.%. As glycols exhibit densities higher than that of water, the addition of those antifreezes usually raises the density difference between dispersed and continuous phases. As a consequence, gravitation phase separation is much more likely, which, in turn, increases the probability of creaming and coalescence destabilizations [42]. Hence, more studies are necessary to explore the design of PCM emulsions based on glycol–water solutions in order to assess their possible use in wider temperature ranges.

This work presents the design of new PCM–in–water and PCM–in–(ethylene glycol+water) nanoemulsions using either *n*–heptadecane or commercial RT21HC paraffin as dispersed phases. The stability of the samples through storage, after freeze–thaw cycles and under mechanical shear was analyzed by visual observation and dynamic light scattering measurements. Phase change characteristics, thermal conductivity and density were experimentally investigated in order to elucidate the influence that dispersed phase drops have on the final thermophysical properties of the PCM emulsions. Finally, the energy storage capacity versus temperature curves of the different prepared emulsions were also presented to define the working temperature range that would allow the best use of the latent heat provided by the PCM drops.

2. Materials and methods

2.1. Materials

Pure *n*–heptadecane, C17, ($T_m = 295$ K, mass purity >99%, Alfa Aesar) and technical grade

RT21HC ($T_m = 294$ K, $\Delta h_m = 152$ J/g, Rubitherm Technologies GmbH, Germany) were used as dispersed phases. According to the supplier of RT21HC [43], the commercial RT-series of phase change materials is based on paraffins and waxes. Two different carrier fluids, *viz.* water and an (ethylene glycol+water) mixture at 20%:80% mass ratio, were utilized as continuous phases. Deionized water was produced with $18.2 \text{ M}\Omega\cdot\text{cm}$ at 298 K by a Millipore system (Billerica MA, USA) and ethylene glycol (mass purity >99%) was purchased from Sigma Aldrich. Hexane (>98.5%, Sigma Aldrich) and sodium dodecyl sulfate, SDS, (98%, Sigma Aldrich) were used as solvent during emulsification and surfactant, respectively. Pure *n*-octacosane, C28, ($T_m = 334\text{--}336$ K, mass purity >99%, Alfa Aesar) and two paraffin waxes, RT55 ($T_m = 328$ K) and RT70HC ($T_m = 343$ K) also from Rubitherm Technologies GmbH, were considered as nucleating agents to try reducing the sub-cooling of the nanoemulsions. Reagents were weighted in a Sartorius analytical balance (Sartorius GmbH, Germany) with an uncertainty of 0.0001 g.

2.2. Emulsion design

PCM emulsions were formulated through the solvent-assisted method proposed by Agresti et al. [20]. First, two solutions, one of PCM(s) in hexane (at a solvent:dispersed phase mass ratio of 1:5) and the other of SDS in water, were joined in an ultrasonic bath at 318 K. Then, the mixture was further sonicated using a VCX130 (Sonics & Materials, Inc., USA) operating at 20 kHz and 65 W with a 12 mm tip. The sample was then stirred at 363 K for 2–3 hours to evaporate the hexane. Finally, water or its mixture with ethylene glycol was added to the emulsion to obtain the desired PCME composition. In this study, emulsions were formulated at PCM mass concentrations of 2 wt.%, 4 wt.% and 10 wt.%, while surfactant content was fixed at a SDS:PCM mass ratio of 1:8. In order to evaluate the effectiveness of C28, RT55 and RT70HC as nucleating agents (NAs) to reduce the sub-cooling effect of emulsions, nano-PCMEs were formulated using a mixture of NA:C17 or NA:RT21HC at 10%:90% mass ratio as dispersed phase. More details about emulsion formulation and the definition of preparation conditions are given in Agresti et al. [20].

Average droplet size, polydispersity and Zeta potential were determined by a Zetasizer Nano ZS (Malvern Instruments Ltd, United Kingdom) equipped with a 4 mW He-Ne laser operating at a wavelength of 633 nm. This device works based on the Dynamic Light Scattering (DLS) technique, which analyzes the time-dependence fluctuations in the intensity of scattered light, by the particle dispersion. Measurements were carried out in the temperature range from 276.15 to 303.15 K with a scattered angle of 173° . In order to obtain representative results, three parallel measurements of 15 runs were conducted for each experiment.

Hydrodynamic sizes, polydispersity indices and Zeta potentials measured by DLS for some of the aqueous nanoemulsions at 298.15 K are gathered in Table 1. More results are summarized in Tables S1–S4 of the Supporting Materials. Nanoemulsions prepared at paraffin contents of 2 and 4 wt.% exhibited average droplet sizes around 90–120 nm, while these values were ~130–150 nm for the samples formulated at 10 wt.%. These average particle sizes were up to 30% smaller than those obtained in some preliminary tests using the formulation previously described but without any solvent. This shows the effectiveness of the solvent-assisted emulsification to produce nanoemulsions with fine PCM drops.

Table 1. Hydrodynamic sizes, polydispersity indices (pdl), Zeta potentials and pH-values obtained at 298.15 K and after preparation for some aqueous nanoemulsions.

Main formulation parameters			Size (pdl)	Zeta Potential	pH
Paraffin (final wt.%)	Solvent (only during emulsification)	Surfactant (final wt.%)			
C17 (2 wt.%)	—	SDS (0.25 wt.%)	142 nm (0.19)		
C17 (2 wt.%)	Hexane	SDS (0.25 wt.%)	115 nm (0.16)	-91 mV	7.8
C17 (4 wt.%)	—	SDS (0.50 wt.%)	148 nm (0.19)	-87 mV	
C17 (4 wt.%)	Hexane	SDS (0.50 wt.%)	105 nm (0.18)	-87 mV	8.1
C17 (10 wt.%)	—	SDS (1.25 wt.%)	200 nm (0.23)		
C17 (10 wt.%)	Hexane	SDS (1.25 wt.%)	140 nm (0.23)	-86 mV	8.4
RT21HC (2 wt.%)	Hexane	SDS (0.25 wt.%)	89 nm (0.14)		
RT21HC (4 wt.%)	Hexane	SDS (0.50 wt.%)	99 nm (0.23)	-82 mV	8.0
RT21HC (10 wt.%)	Hexane	SDS (1.25 wt.%)	127 nm (0.24)		

Owing the thermodynamically unstable nature of PCM emulsions, destabilization is a main concern during sample formulation [11,44]. Different factors such as temperature, storage time, droplet freezing or mechanical shear stress may negatively affect sample stability [11,18,24]. For that reason, a careful analysis considering these variables is always necessary. First, DLS measurements were performed at different temperatures (in the range from 276.15 K to 303.15 K) for several samples (Table S1 of Supporting Materials). Changes in average droplet size within experimental uncertainty of the device were observed when the dispersed phase was solid, liquid or while the PCM underwent the solid–liquid transition (around 293 K). As an example, Figure 1a shows the size distributions obtained at different temperatures for the water–based nanoemulsion prepared at a C17 concentration of 10 wt.%.

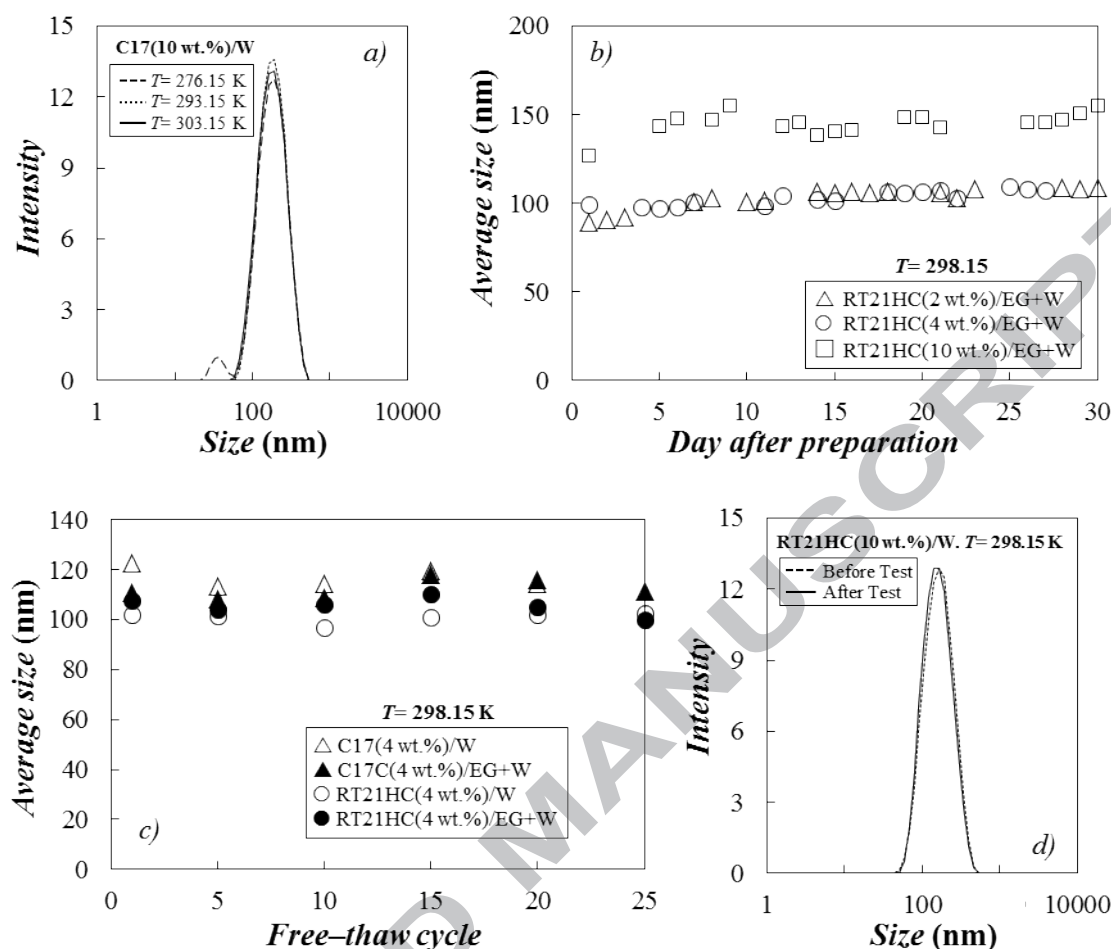


Figure 1. (a) Size distributions at different temperatures, (b) temporal evolution of droplet mean diameter, (c) changes in droplet average size after freeze–thaw cycling and (d) size distributions before and after the mechanical shear stress test for some representative samples.

In order to assess the stability of the samples through storage, size measurements at 298.15 K were repeated for at least a month (Tables S2 and S3 of Supporting Materials). Figure 1b shows the changes in droplet size for three RT21HC–emulsions prepared using the (ethylene glycol+water) mixture as carrier fluid. It can be observed as the average size slightly increased during the first days and then remained quite constant. Simultaneously, most of the samples exhibited a small reduction in polydispersity index, which may be due to the fusion of small drops with larger ones [15]. Similar results were found for water– and (ethylene glycol+water)–based PCMEs, which indicates that the addition of the glycol did not alter the good stability of the nanoemulsions. This indicates that nanoemulsions were fine enough so that Brownian movement could ensure PCM droplets movement throughout the sample (avoiding their accumulation at the top) [42]. As shown in Figure 1c for the C17(4 wt. %) and RT21HC(4 wt. %) nanoemulsions based on water and (ethylene glycol+water) mixture, no increase in droplet size was observed after 25 freeze–thaw cycles covering the temperature range between 277 K to 303 K (Table S4 of Supporting Materials). Finally, no demulsification evidences were detected when the RT21HC(10 wt. %)/W sample was

subjected to a mechanical shear for 6 hours at temperatures of 283.15 K (solid PCM droplets) or 303.15 K (liquid PCM droplets), see Figure 1d.

Zeta potential measurements were carried out at 298.15 K for some representative emulsions using the Zetasizer Nano ZS device, which determines this property from the electrophoretic mobility by laser Doppler velocimetry. Absolute Zeta potentials over 30 mV are usually an indication that electrostatically repulsive charges among drops are strong enough to prevent agglomeration and coalescence. In our case, negative values larger than -71 mV were found for either water- or (ethylene glycol+water)-based PCMEs. Measured Zeta potentials were similar to those reported by Puupponen et al. [15] or Agresti et al. [20] for PCMEs formulated using SDS, while they double in value the results obtained by Jadhav et al. [45] for emulsions prepared utilizing this same surfactant. The pH-values of designed nanoemulsions (measured with a pH-Meter Crison GPL-21 and a pH-electrode code 5011-T) are in the range of 7.8–8.4.

2.2. Thermophysical properties

Phase change transitions were experimentally studied in the temperature range from 243 K to 333 K using a heat-flux Differential Scanning Calorimeter (DSC) Q2000 (TA Instruments, New Castle, USA) equipped with a refrigerated cooling system RSC90. Samples of about 2 mg (in the case of bulk *n*-heptadecane and RT21HC) or 10 mg (for the nanoemulsions) were placed in alodine-aluminium crucibles and sealed with hermetic lids. Cells were weighted (in a Mettler AE-240 electronic balance with an accuracy of $\pm 5 \cdot 10^{-5}$ g) before and after the tests in order to verify that no mass change had occurred during the studies. Experiments were carried out at scanning rates ranging from $\beta = 1$ to 5 K/min (except for the bulk-PCMs for which only $\beta = 1$ K/min was considered) using a three-run method: *i*) empty cell, *ii*) synthetic sapphire disk (standard reference material) and *iii*) sample [46]. In order to verify the repeatability of measurements, sample runs were repeated at least three times. Besides, the process was performed for at least two different aliquots of each emulsion/bulk PCM. A constant stream of nitrogen (flow rate: 50 ml/min, N₂ molar fraction purity > 0.99999) was flushed through the DSC chamber to create an inert atmosphere environment. Estimated uncertainties for transition temperatures and enthalpies are 0.3 K (with a repeatability of 0.1 K) and 1.2 J/g (with a repeatability of 0.7 J/g), respectively [47].

Thermal conductivities were obtained at temperatures ranging from 275 K to 333 K by means of a hot disk thermal constants analyzer model TPS 2500 (Hot Disk AB, Sweden). This device is based on the transient plate source technique and is appropriate for determining the thermal conductivity of liquids, solids and powders in the range from 0.005 to 500 W/(m·K). A 7877 sensor consisting of a nickel wire wound in a double spiral pattern with a radius of 2 mm and covered with

Kapton was selected for the studies. In the case of solid bulk-RT21HC measurements, the probe was horizontally placed between two bricks of sample with parallel plane surfaces to ensure complete contact between sensor and paraffin wax. The assembly was introduced in a thermostatic air chamber for temperature control. For liquid bulk-C17, bulk-RT21HC and nano-PCMEs measurements, the sensor was vertically immersed in the sample, which completely surrounded the sensor so that heat could freely diffuse in all directions. Both sample and probe were contained in a specially build block maintained under isothermal conditions using a thermostatic oil bath. Low thermal powers (up to 30–40 mW) with input times of 4 s (liquid samples) and 40 s (solid bulk-RT21HC) were utilized. At least four different tests were performed for each sample and condition to verify that measured values did not deviate from each other. The declared instrument uncertainty is 5%, however, previous tests performed on stainless steel and deionized water revealed percentage absolute average deviations less than 2% [48,49].

Density was measured in the temperature range from 288.15 K to 303.15 K by an oscillating U-tube densimeter DMA 500 (Anton Paar, Austria). The device was calibrated measuring water and toluene as reference material at the same experimental temperatures of the studied samples [50]. The estimated relative uncertainty of the density measurements was established to be lower than 0.1% [51].

3. Results and discussion

3.1. Phase change characteristics

Temperatures and enthalpies associated to crystallization and fusion thermal events were characterized by differential scanning calorimetry. Cooling and heating thermograms of bulk-C17, bulk-RT21HC and phase change emulsions prepared without any nucleating agent are presented in Figures 2–3. More results are summarized in Tables S5–S8 of the Supporting Materials.

In heating process, bulk-C17 showed two endothermic peaks close to each other but clearly differentiated (Figure 2b). As well documented in literature for different paraffins with an odd-number of carbons such as *n*-heptadecane, these two peaks are consequence of an intermediate disordered phase between the ordered orthorhombic crystalline structure and the isotropic liquid phases [52,53]. The peak at lower temperature ($T_m = 283.8$ K, $\Delta h_m = 43.7$ J/g) corresponds to the crystalline-rotator phase transition, while the peak at higher temperature ($T_{C-R} = 294.5$ K, $\Delta h_{C-R} = 160.9$ J/g) is the rotator phase-liquid transition (melting). Latent heats reported here deviate less than 4% from previous literature values [52–54]. Likewise, the cooling DSC curve of *n*-heptadecane (Figure 2a) exhibits two main exothermic peaks which correspond to the opposite

processes, *i.e.* liquid–rotator phase transition ($T_{L-R}= 293.5$ K) and rotator–crystalline phase transition ($T_{R-C}= 282.5$ K).

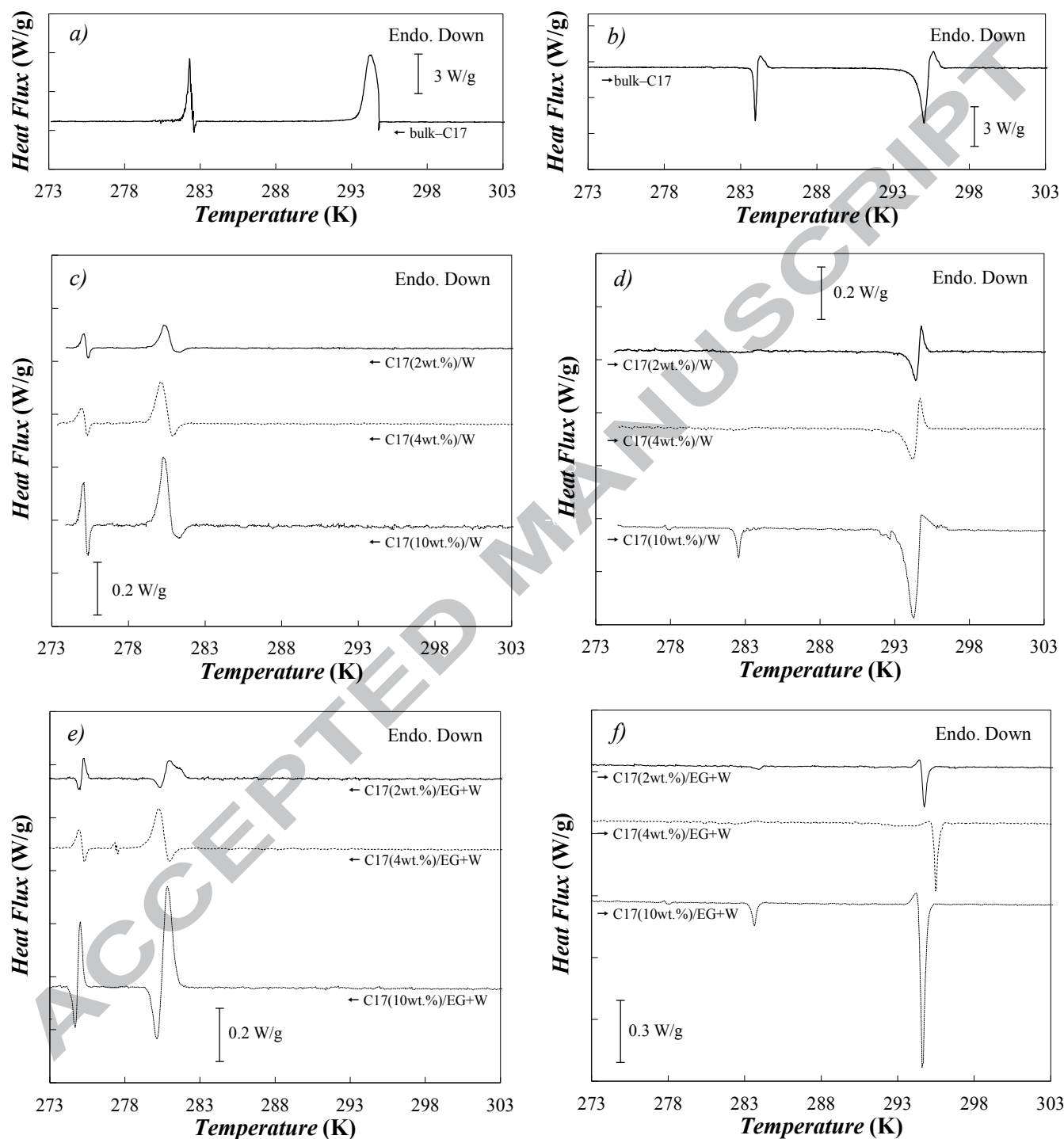


Figure 2. (a,c,e) Cooling and (b,d,f) heating DSC curves obtained at 1 K/min for bulk-C17 and C17-nanoemulsions.

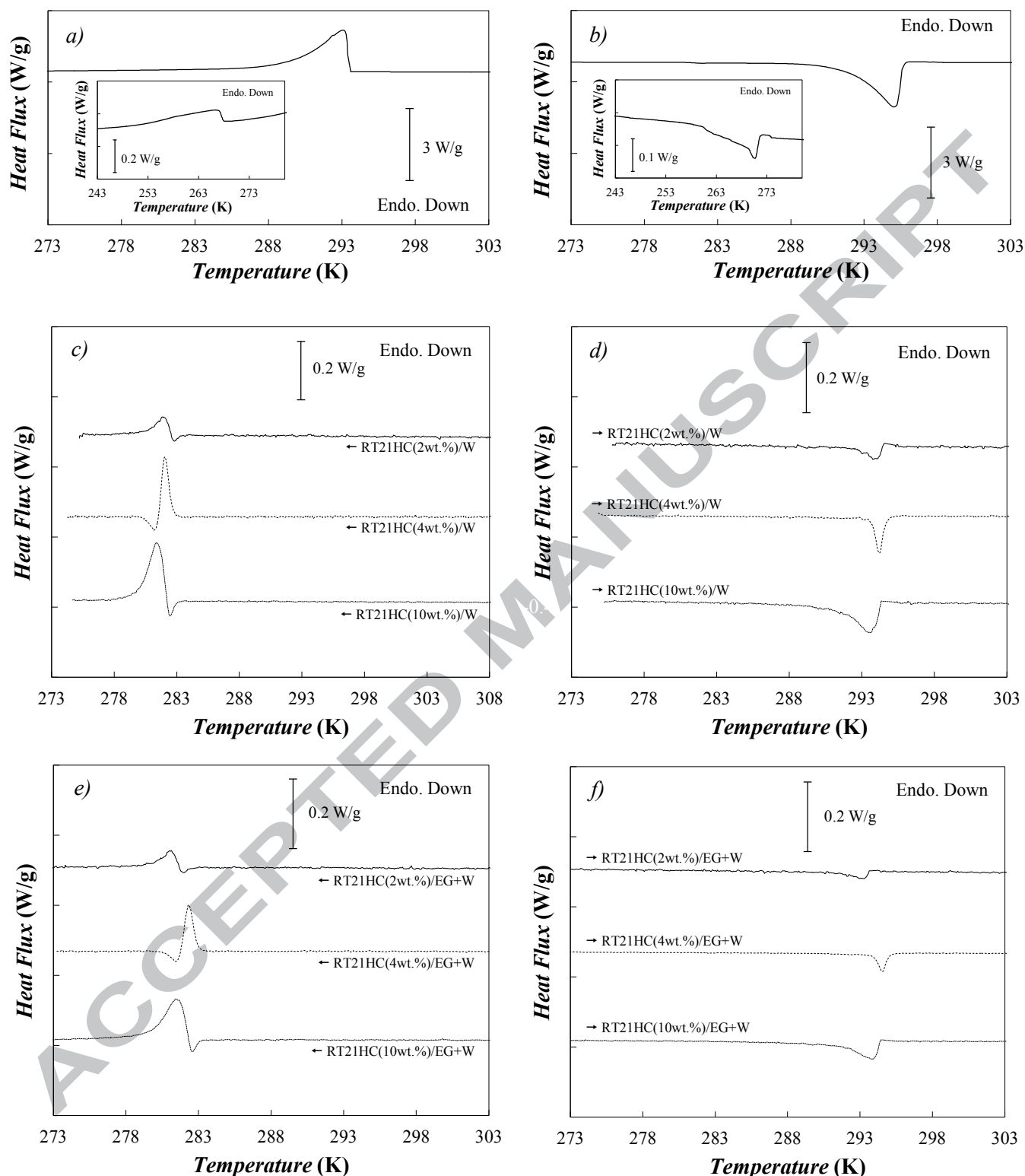


Figure 3. (a,c,e) Cooling and (b,d,f) heating DSC curves obtained at 1 K/min for bulk-RT21HC and RT21HC-PCMEs.

Two peaks were also observed in the thermograms of bulk-RT21HC (Figures 3a and 3b). To facilitate visual comparison between bulk-RT21HC and nanoemulsion thermograms, peaks occurring at temperatures lower than 273 K were presented in insert figures. The wide peak observed in the DSC heating curve of RT21HC (Figure 3b (inside)): $T_{S-S,peak} = 267.4$ K and $\Delta h_{S-S} =$

16.4 J/g) corresponded to a solid–solid transition, while the peak at higher temperature (Figure 3b: $T_m = 293.3$ K and $\Delta h_m = 142.7$ J/g) was the melting phase change. The complex polymorphic nature of different alkane binary mixtures is quite common and depends on molecular length, parity or composition [54–56]. Besides, a similar two–peaks behavior was also reported in literature for other commercial paraffinic PCMs such as RT21 [57,58] or RT25 [59], for example. Since the solid–solid phase change of the RT21HC was not within the temperature range in which water and the (ethylene glycol+water) mixture used as continuous phase are liquid, this transition was not considered hereafter.

In the case of PCM nanoemulsions, it can be observed as the onset of the melting temperature is $\sim 1\text{--}3$ K lower than the corresponding bulk–PCMs. This shift of melting transition towards lower temperatures was previously attributed to the increased free energy of PCM droplets, consequence of a higher surface to volume ratio [15]. The melting enthalpy of nanoemulsions rises with the increasing fraction of dispersed phase. However, these latent heats are about 12–37% lower than the values expected according to the following mass relation:

$$\Delta h_{lat,PCME} = \phi_{PCM} \cdot \Delta h_{lat,PCM} \quad (1)$$

Good agreement between experimental DSC measurements and theoretical predictions, with deviations lower or equal to 8.5%, were reported by Cheng and Zhang [60] for *n*–hexadecane and *n*–octacosane nanoemulsions. However, enthalpies up to 20% lower than predicted by Eq.(1) were also obtained by Zhang et al. [18] when studied aqueous emulsions of *n*–octacosane formulated by using different high–energy preparation methods. Reductions in the heat of fusion were also reported by different authors when studied substances such as helium, organic fluids, water and metals enclosed in nanopores [61]. In particular, Mu and Malhotra [62] found decreases up to 82% in melting heat studying cyclohexane confined in Spherosil glass with pore sizes ranging from 4 nm to 62.5 nm. Authors found that the narrower the pores, the larger the reduction in latent heat. For that reason, they attributed this decrease to the non–participation in the phase transition of molecules adjacent to the pore walls.

In the DSC heating thermograms of C17–nanoemulsions, it was also possible to detect the crystalline–rotator phase transition of PCM droplets, as Sari et al. [63] also observed for *n*–heptadecane micro/nano–capsulated with polystyrene [63] or polymethyl methacrylate [64]. Like with melting, solid–solid transition of PCMEs also occurred at slightly lower temperatures than for the bulk–C17. Enthalpies associated to the solid–solid transition were up to 59% lower than the values calculated from Eq.(1). Rotator phases are characterized by high levels of rotational and conformational disorder [54]. In the case of alkanes embedded in small pores, different authors

[65,66] have found that confinement destroys the lamellar arrangements of alkane molecules reducing rotational freedom around the molecular axis. Hence, the difference between predicted and experimental latent heats of crystalline–rotator phase transition (larger than in the case of melting transition) could also be due to the distortions of alkane chains because of a higher molecular packing in the PCM drops or a possible high defective nature of formed crystals. In the case of the PCM emulsions studied in this work, this idea could be supported by the fact that latent heat reduction was more perceptible at 2 wt.% and 4 wt.% paraffinic loads (for which PCM drops were smaller in size) than for the 10 wt.%. However, the reduced area of the peaks, particularly at low concentrations and scanning rates, makes difficult an accurate characterization of crystalline–rotator phase transitions. Thus, a further interpretation of results was not possible.

More noticeable shifts in temperature could be observed when comparing cooling thermograms of bulk–PCMs and nanoemulsions. Thus, while the liquid–solid phase temperatures (freezing onsets) of bulk–C17 or bulk–RT21HC were only ~2 K lower than the melting onsets (sub–cooling phenomena), this difference reached 13 K in the case of some nanoemulsions. Large sub–coolings, between 9 and 15 K, were also found in the literature [21] for paraffin–in–water nanoemulsions stabilized with SDS or other surfactants. This behavior is consequence of the fact that foreign nucleation sites, which usually trigger heterogeneous nucleation in the bulk–PCM, are distributed among a large number of isolated PCM drops in the case of the PCM emulsions.

In order to reduce this undesirable effect, three PCMs (C28, RT55 and RT70HC) with melting points higher than the material in solidification (C17 or RT21HC) were considered as nucleating agents (NAs). In all cases, the NA:C17 or NA:RT21HC mass ratio was fixed at 10%:90% except for the C28:C17 combination, for which a ratio of 5%:95% was also analyzed. Figures 4 and 5 show the DSC curves obtained for the aqueous emulsions prepared at a dispersed phase concentration of 4 wt.% with and without nucleating agent. The four paraffinic NAs tested with C17– and RT21HC–nanoemulsions only led to partial reductions of the sub–cooling effect. A comparison between DSC thermograms of C17–in–water nanoemulsions prepared with and without nucleating agents showed maximum reductions in sub–cooling phenomenon of 3.2 K (RT55), 2.5 K (C28) and 2.3 K (RT70HC). Similar results were also found for RT21HC–in–water nanoemulsions, for which maximum diminutions in sub–cooling were 3.0 K (RT55) and 2.3 K (RT70HC). These reductions were considerably lower than our initial expectations since the nanoemulsions prepared with NAs still present quite large sub–cooling effects, 9.9–10.5 K for C17–samples and 7.4–9.5 K for RT21HC–samples. In the case of C17–PCMEs containing RT70HC as nucleating agent, a three–peak behavior was observed during the cooling scans (to ease identification of the third peak, it was marked with an arrow in Figure 4a). Spectra of several freezing peaks were reported in the

literature for different PCM slurries containing paraffinic nucleating agents [21,67]. The first-order phase transition at higher temperature during the cooling process was attributed to the existence of differences in the types of seeds which promote nucleation in the PCM drops [22].

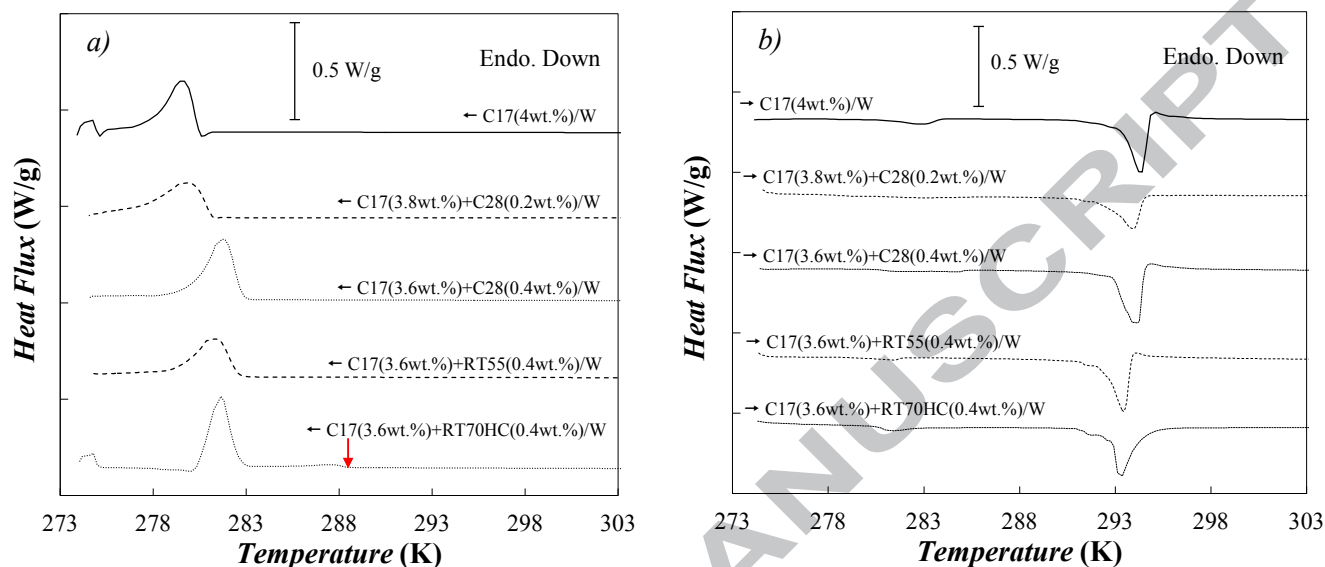


Figure 4. (a) Cooling and (b) heating DSC thermograms obtained at 5 K/min for several C17-emulsions prepared with and without nucleating agent.

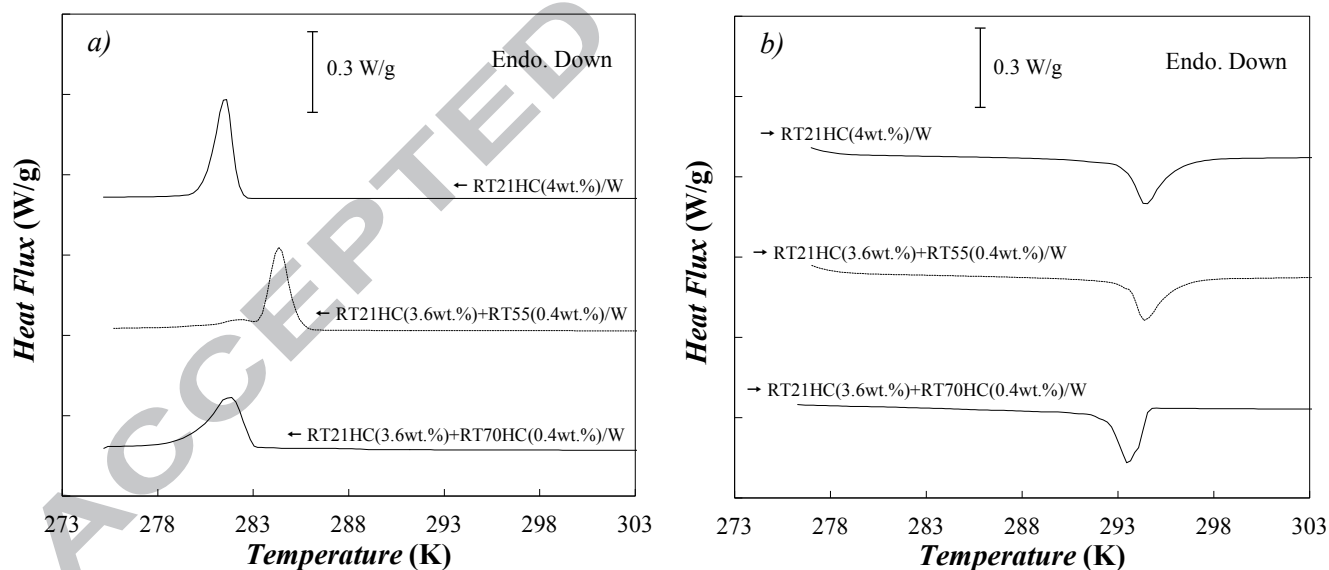


Figure 5. (a) Cooling and (b) heating DSC thermograms obtained at 5 K/min for RT21HC-emulsions prepared with and without nucleating agent.

As done by Kousksou et al. [68], experiments were carried out at different cooling rates to evaluate whether scanning conditions had any influence on thermodynamic or kinetic properties of the crystallization and melting behavior of PCMEs. No significant differences in enthalpy or temperature were observed between the results. They are reported in Figures 2-5 or Tables S5-S8 of Supporting Materials within the studied scanning rate range.

3.2. Enthalpy temperature curves and heat storage capacity

Cooling/heating enthalpy versus temperature curves can be obtained by integrating DSC heat flux signals [36,69]. As an example, Figure 6a shows the heating thermogram and the fusion enthalpy curve for RT21HC(10 wt.)/W sample, while Figure 6b plots the total stored energy for C17(10 wt.)/EG+W. Given the latent heat released/absorbed by PCM drops during their crystallization/fusion, nanoemulsions provide increases in heat storage at temperatures around those phase change transitions. However, as it can be observed in the following expression, total stored thermal energy does not only depend only on the latent heat provided by PCM drops, but also on the temperature range covered by the thermal fluid (sensible heat) [32,36].

$$\Delta h = \varphi_{PCM} \cdot \Delta h_{lat,PCM} + (\varphi_{PCM} \cdot c_{p,PCM} + (1 - \varphi_{PCM}) \cdot c_{p,CF}) \Delta T \quad (2)$$

As assumed in [36], isobaric heat capacities of surfactant and nucleating agents were not considered given their minor contributions to the total heat storage capacity. Figure 7 presents the enhancement in heat storage capacity (regarding the carrier fluid used as continuous phase) of different C17– and RT21HC–nanoemulsions formulated without any nucleating agent. Calculations were made by using latent heat results reported in Tables S5 and S6 of Supporting Materials. In the case of C17–PCMEs, only thermal energy associated to melting transition was considered. As can be observed in Figure 7, the smaller the temperature interval in which the material works, the larger the enhancement in stored thermal energy. Considering an ideal ΔT (ΔT = sub-cooling, that would be the minimum temperature interval to cover by the PCME so that the PCM drops reversely undergo the solid–liquid phase transition), the maximum enhancements in heat storage capacity would be 16% and 26% for C17– and RT21HC–nanoemulsions prepared at 10 wt.% PCM concentration in the (ethylene glycol+water) mixture. This evidences the importance of limiting the sub-cooling of phase change material nanoemulsions to really profit the latent heat provided by the PCM drops.

Figure 8 shows the enhancements in the heat storage capacity of C17– and RT21–aqueous emulsions prepared with a total amount of dispersed phase of 4 wt.% with and without nucleating agent, considering an ideal temperature interval equal to their sub-cooling, *i.e.* ΔT = sub-cooling. In this case, despite the lower latent heats of the nanoemulsions which contain nucleating agent (in comparison to the samples prepared without NA), the lower sub-cooling effect of these nanoemulsions leads to slightly better heat storage capacities. This strengthens the great importance of continuing working on the reduction of the sub-cooling effect of PCM nanoemulsions.

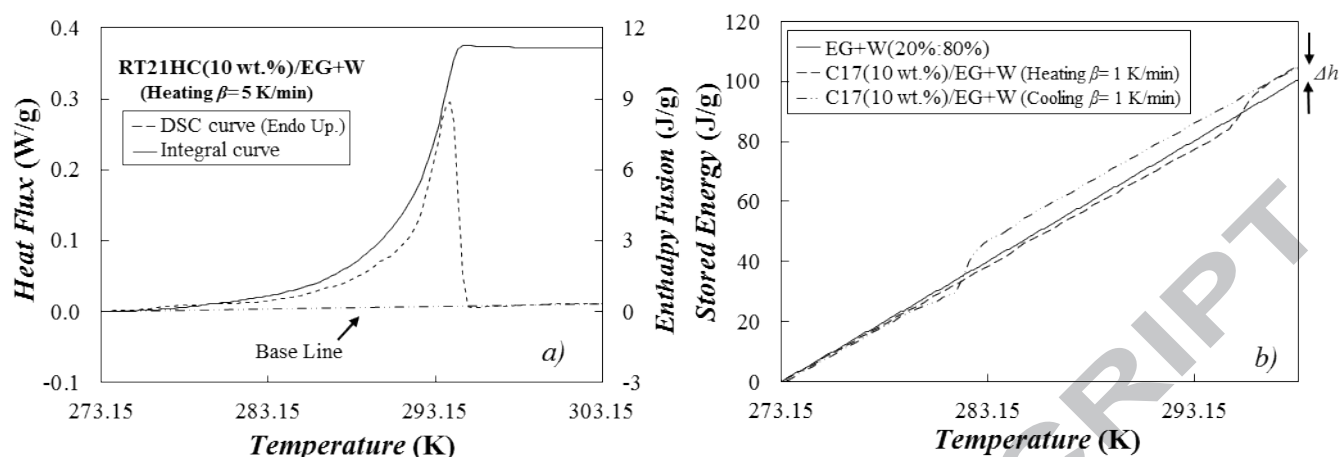


Figure 6. DSC melting curve and integral curve of RT21HC(10 wt.)/W emulsion and b) total stored energy of C17(10 wt.)/EG+W sample compared to that of the base fluid.

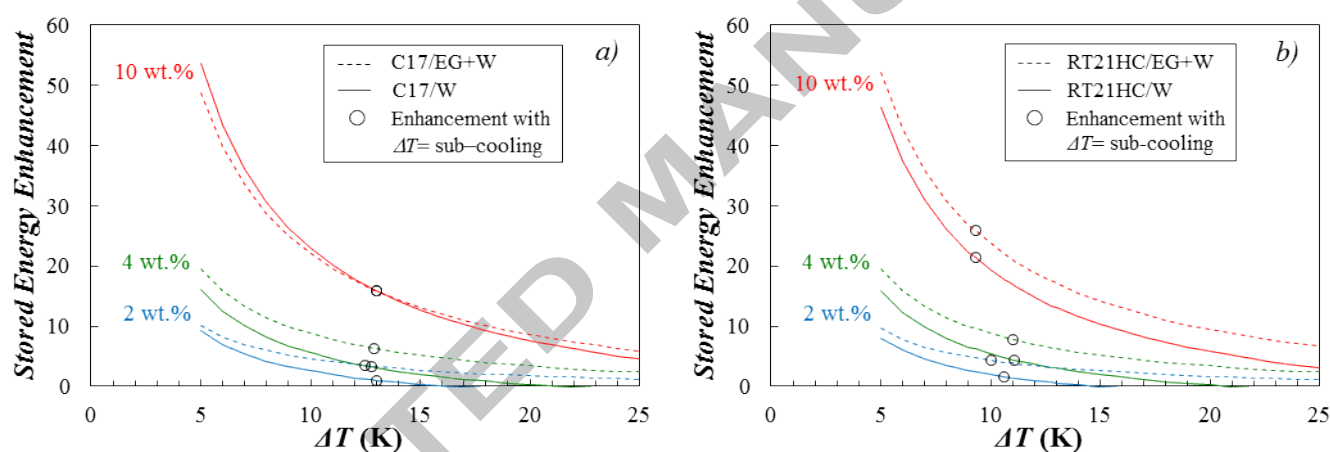


Figure 7. Enhancements in heat storage capacity as a function of the temperature interval covered by the thermal fluid, ΔT , for nanoemulsions prepared without nucleating agent.

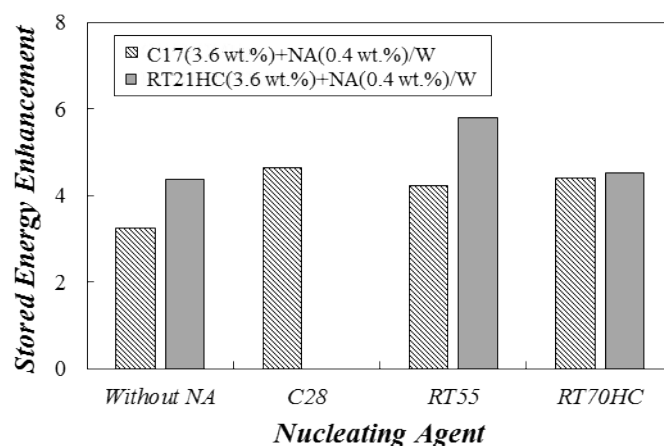


Figure 8. Enhancements in heat storage capacity obtained with and ideal $\Delta T = \text{sub-cooling}$ by aqueous nanoemulsions prepared with different nucleating agents (NA).

3.3. Reliability after storage/cycling and droplet resistance against carried fluid freezing

Like for any other latent heat storage material, the cycling reliability of PCM emulsions must be carefully evaluated to ensure that designed materials will maintain their good thermal performance in the long term [70]. Lu et al. [41] studied the effects of storage and thermal cycling on the freezing and melting temperatures of an aqueous emulsion prepared at a RT6 paraffin concentration of 40 wt.%. A comparison of the cooling thermograms obtained for that sample fresh made and 8 months after its formulation showed that, while the onset of freezing transition remained almost unaffected, a small portion of material exhibits now a slightly large sub-cooling. However, this secondary peak disappeared from DSC curves after cycling the sample for 50 freezes–thaws. Huang et al. [35] compared the DSC scans measured for a RT10–in–water emulsion (30 wt.% of paraffin) just after preparation and 16 months later. In this case, authors did not find any noticeable difference between the two thermograms, which would probe the storage reliability of samples. In our study, two different tests were performed with the objective of analyzing the storage/cycling reliability of designed emulsions. Firstly, the just prepared nanoemulsions containing 4 wt.% of either C17 or RT21HC in W and EG+W were subjected to 100 cooling–heating cycles at a scanning rate of 10 K/min. No appreciable differences were found between the first and last freeze–thaw cycles for any of the four samples (Figure 9a). After nine months, the RT21HC–in–water emulsion was subjected to a second cycling test during 1000 freezing–melting processes (Figure 9b). In this second experiment, freezing and melting onset temperatures were similar to those of the original test (Figure 9a). However, freezing peak is now narrower and slightly larger in area (just after preparation: $\Delta h_m = 4.35$ J/g vs. 8 months later: $\Delta h_m = 4.79$ J/g), which may be a consequence of a slight increase in droplet size and a reduction in polydispersity index. In this second cycling test, no significant change was observed in DSC curves throughout thermal cycles.

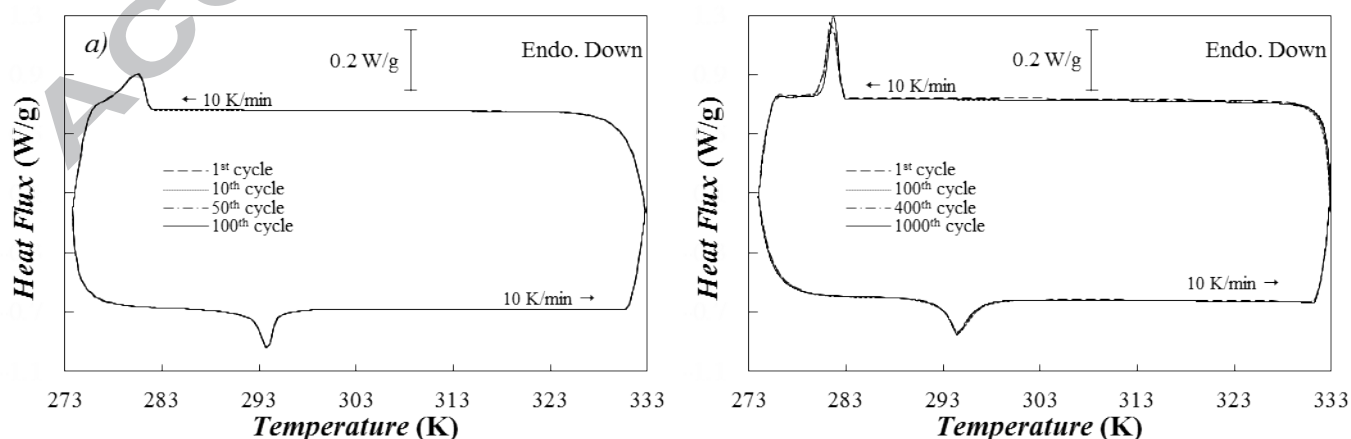


Figure 9. Freeze–thaw cycling tests for RT21HC(4 wt.)/water emulsion a) just after preparation and b) 9 months after preparation. Obtained DSC curves for the different runs are superimposed.

In order to analyze the resistance of PCM drops against the freezing of the carrier fluid used as continuous phase, some nanoemulsions were cooled several times down to ~ 243 K. As an example, Figure 10 shows the photos of C17(4 wt.%)–nanoemulsions in water and the (ethylene glycol+water) mixture taken before and after carrier fluid solidification. In the case of aqueous samples, nanoemulsions were destabilized after being cooled below the freezing point of water (evidences of phase separation can be observed at the top of the vial). However, nanoemulsions seemed to resist this process when the ethylene glycol was present in the sample. With the aim of confirming that no alteration in the phase change characteristics of PCM drops occurred after solidification of the continuous phase, additional DSC scans covering temperatures from 223 to 333 K were also performed for some PCMEs. The scans of the nanoemulsions prepared using 4 wt.% of *n*-heptadecane in water and (ethylene glycol+water) are also presented in Figure 10. No significant change in solidification process was observed between the first and second (or successive) cooling curves of the nanoemulsion based on (ethylene glycol +water), Figure 10d. This contrasted with the behavior of aqueous nanoemulsions for which the solidification peaks shift to considerably higher temperatures (similar to those of the bulk–PCM), indicating that disperse and continuous phases separated.

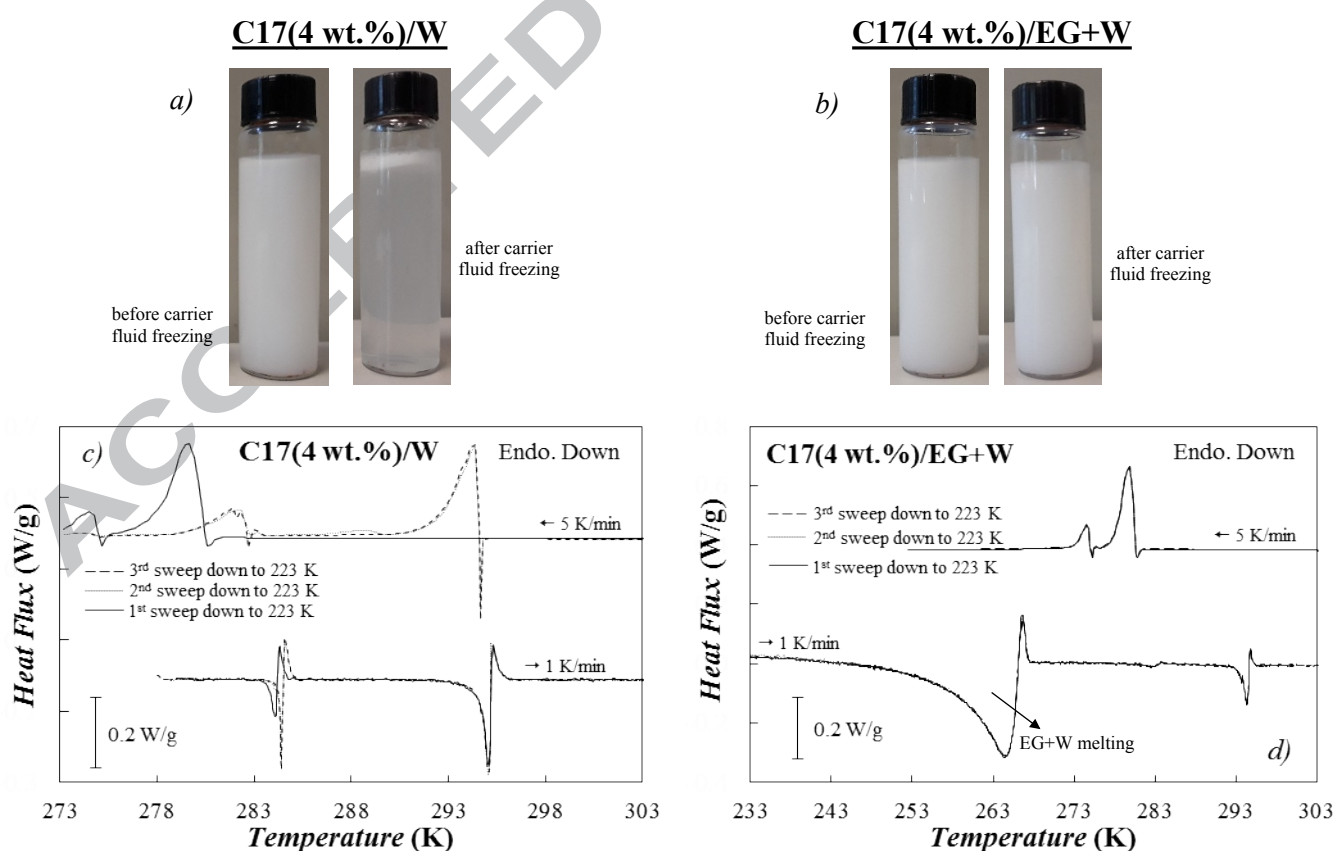


Figure 10. Droplet resistance against carrier fluid freezing: (a,b) visual appearance and (c,d) DSC thermograms.

3.4. Thermal conductivity

Experimental thermal conductivity obtained for bulk-C17, bulk-RT21HC, water, the (ethylene glycol+water) mixture and PCM nanoemulsions are plotted in Figure 11. Measured k value for bulk-C17 in liquid phase was 0.149 W/m·K (at 303 K), which is in agreement with the value of 0.146 W/m·K (at 303 K) reported by Vélez et al. [52]. In the case of bulk-RT21HC, thermal conductivity in solid (at 283 K) and liquid (at 303 K) states were 0.207 W/m·K and 0.153 W/m·K, respectively. Results obtained here for the two fluids used as continuous phases agreed with those previously reported in literature, showing $AADs\%$ of 1.1% with Refprop 9.0 [50] in the case of water and 1.2% with Melinder [71] for the (ethylene glycol+water) mixture.

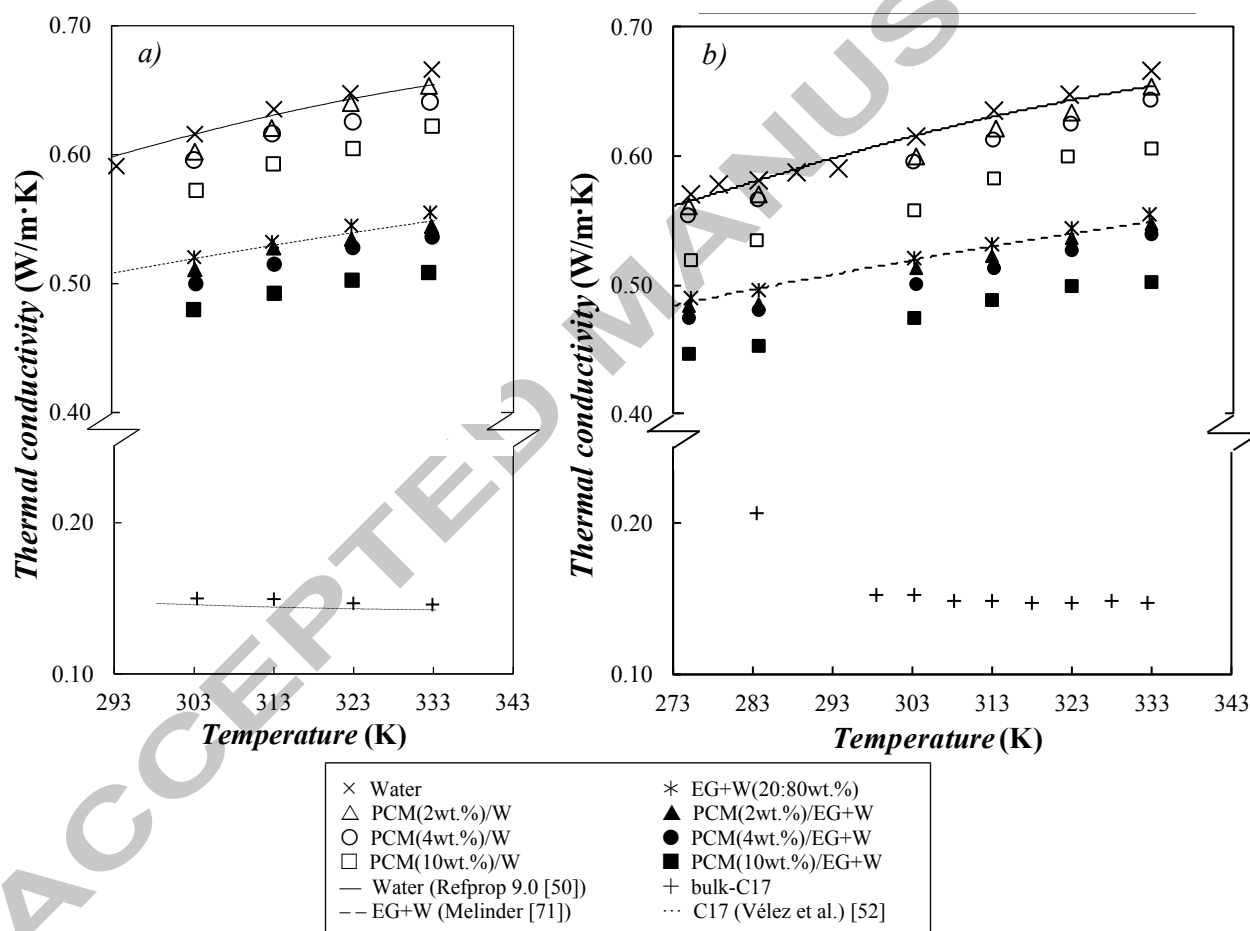


Figure 11. Experimental thermal conductivity of (a) C17 and (b) RT21HC sets at different temperatures.

As expected, PCM emulsions exhibited apparent thermal conductivities lower than those of the fluids used as continuous phase. This is due to the fact that the thermal conductivities of C17 and RT21HC (dispersed phases) are also lower than those of carrier fluids. Average reductions in this property up to 9.4% were obtained at the highest PCM concentration (10 wt.%). No appreciable differences in k were observed when part of dispersed n -heptadecane or RT21HC was replaced by a PCM with higher melting point (nucleating agent).

Assuming that PCMEs are low-concentration dispersions of non-interacting spheres, the apparent thermal conductivity of the nanoemulsions can be predicted by the Maxwell equation [72]:

$$k_{PCME} = k_{CF} \frac{k_{PCM} + 2 \cdot k_{CF} + 2 \cdot \phi_{PCM} \cdot (k_{PCM} - k_{CF})}{k_{PCM} + 2 \cdot k_{CF} - \phi_{PCM} \cdot (k_{PCM} - k_{CF})} \quad (3)$$

As an example, Figure 12 shows the reductions in thermal conductivity experimentally measured for RT21HC/EG+W nanoemulsions together with the values predicted by Maxwell model [72]. Similar results to those here presented for (ethylene glycol+water)-based emulsions were also observed for water-based systems.

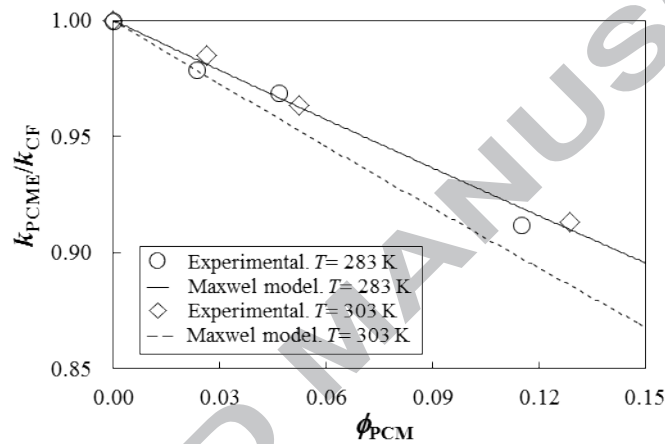


Figure 12. Relationship between thermal conductivity ratio, k_{PCM}/k_{CF} , and PCM volume concentration, ϕ_{PCM} , for RT21HC/EG+W nanoemulsions.

When PCM droplets were in solid phase, Maxwell equation [72] seemed to predict quite well the reductions in thermal conductivity as a function of the dispersed phase volume fraction. However, Eq. (3) underestimated the experimental results when PCM droplets were liquid. These differences were more appreciable at high temperatures and large RT21H contents, for which experimental and predicted values deviated up to 6%. Maximum differences were detected at the higher temperatures and for the highest concentration. There is evidence in literature of the reasonable validity of Maxwell equation for non-nanoscale particle suspensions of low volume fractions [73]. Good predictions were also reported when that model was applied with some nanoemulsions. Thus, Saarinen et al. [74] studied the thermal conductivity of *n*-decane-in-water emulsions (droplet diameter ~100 nm) and micelles-in-water fluids (using Tween 20 and SDS as surfactants with sizes ~6 nm) and experimental results did not significantly deviate from values calculated by using Maxwell equation. A good agreement between experimental thermal conductivities and the values predicted by using Maxwell model were also found by Morimoto et al. [13,75] for aqueous phase change emulsions prepared by D-phase emulsification and containing either *n*-hexadecane or *n*-hexadecane droplets (10–30% in mass) with diameter sizes ~223–246 nm. Conversely, different

studies reported that Maxwell model considerably deviates from empirical results for several nanodroplet suspensions. For instance, Sul et al. [76] analyzed the thermal conductivity of *n*-heptadecane nanoemulsions based on water and a H₂O/LiBr binary mixture as a function of paraffin concentration and surfactant used in sample stabilization. Experimental thermal conductivities up to 6.4% higher than values predicted by Maxwell model were observed for a paraffin-in-water nanoemulsion containing 0.1 wt.% of *n*-decane droplets (~75 nm in size). Higher experimental values than predicted by Eq.(3) were also recently reported by Liu et al. [77] when studied water-based emulsions designed using 1–4 wt.% of liquid oil droplets (0.6–8.5 μm in size). These differences, attributed to additional scale-dependence phenomena, are not considered by the classical Maxwell model, such as interfacial resistance, Brownian motion, droplet/carrier fluid interactions or emulsion-lade flow, which can appear depending on nanoparticle size, the content of dispersed phase and/or temperature [11,76,78]. These phenomena may be more noticeable when PCM droplets are in liquid phase, for which the assumption of non-interactive nano-size droplets may be wrong.

3.5. Density

Density was experimentally obtained for pure *n*-heptadecane and bulk-RT21HC in the temperature range from 296.15 K to 303.15 K, while for the (ethylene glycol+water) mixture and PCM nanoemulsions it was measured in the interval from 288.15 K to 290.15 K. This property is not only necessary to assess the storage energy density of PCMEs, but also provides information about the volume changes experienced by the emulsions as a consequence of temperature and droplets phase change [37]. The value measured in this work at 303.15 K for pure C17 deviated less than 0.05% from literature data [79,80]. A good agreement, with an *AAD*% of 0.09%, was also found between our densities and results reported by Melinder et al. [71] for the (ethylene glycol+water) mixture (20%:80% in mass). Figure 13a shows the temperature evolution of density for C17-in-water emulsions prepared at different concentrations of dispersed phase. Nanoemulsion densities reduce with increasing concentration of PCM. Maximum diminutions reached 2.5% in the case of water-based samples and 3% for (ethylene glycol+water) systems. Similar temperature trends in density were obtained for both the carrier fluid used as continuous phase and nanoemulsions at temperatures lower than 290 K or higher than 296 K. However, a noticeable change in ρ was observed for nanoemulsions around the melting temperature of the PCM drops. These variations around the melting transition (overcoming 1% in only 6 K for the nanoemulsions prepared at the highest PCM concentrations) are due to the volumetric expansion of the PCM as a consequence of the phase change from solid to liquid.

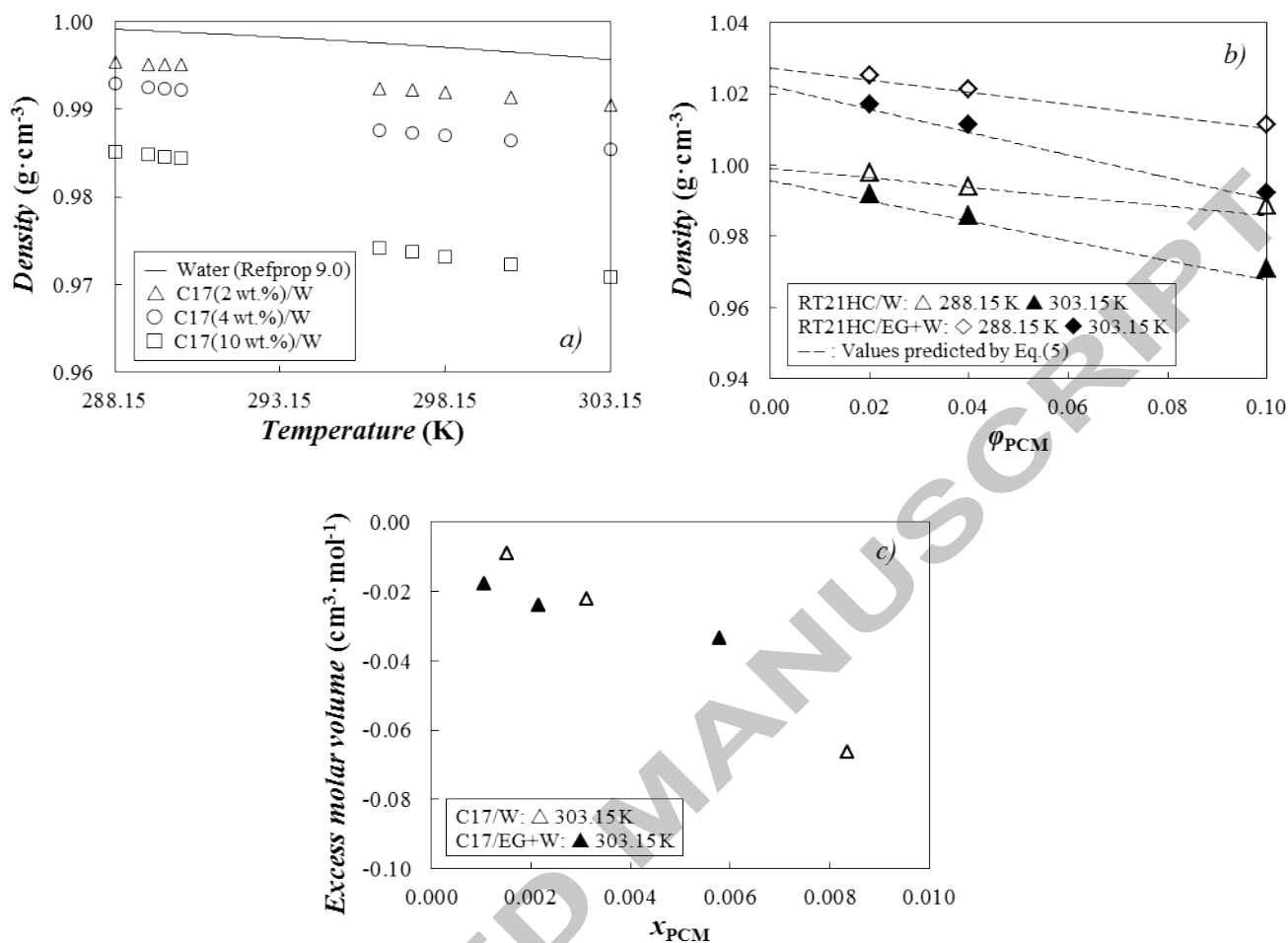


Figure 13. (a) Temperature dependence of density for C17/W nanoemulsions, (b) concentration dependence of density for RT21HC-nanoemulsions and (c) excess molar volume for C17-nanoemulsions.

Isobaric thermal expansivity, α_p , also known as cubical expansion coefficient, can be obtained from numerical differentiation of density–temperature curves by using the following expression:

$$\alpha_p = -(1/\rho)(\partial\rho/\partial T)_p \quad (4)$$

In this case, densities of PCMEs were described as a function of temperature by using two second-order polynomial fittings, one for $288.15 \text{ K} \leq T \leq 290.15 \text{ K}$ (solid paraffin droplets) and the other for $296.15 \text{ K} \leq T \leq 303.15 \text{ K}$ (liquid droplets), while one single adjustment was considered in the entire analyzed temperature range for bulk paraffins and the (ethylene glycol+water). Similar $\alpha_p \approx 8.8\text{--}8.9 \cdot 10^{-4} \text{ K}^{-1}$ were obtained for *n*-heptadecane and RT21HC at 303.15 K. Obtained values agree with those previously reported for other *n*-alkanes [81,82]. Table 2 compares isobaric thermal expansivities calculated for PCMEs at the highest paraffin loadings and the carrier fluids used to formulate them. α_p increases with the paraffin content in the sample. This variation is more noticeable in the case of the aqueous emulsions at 289 K (due to the lower isobaric thermal

expansivity of water at that temperature). The effect of PCM loading on α_p coefficient of phase change material suspensions has not been extensively studied, especially under the phase change. Therefore, to the best of our knowledge, only Wang et al. [83] have performed this kind of studies for water suspensions of micro-encapsulated propanol. In that investigation, authors observed that α_p multiplied its value by six during melting transition.

Table 2. Isobaric thermal expansivities, α_p , calculated for the carrier fluids and PCMEs formulated at the highest paraffin loadings.

Droplet Material (wt.%)	$10^4 \cdot \alpha_p$ (K ⁻¹)			
	W-based PCMEs		EG+W (20%:80%)-based PCMEs	
	$T=289.15$ K	$T=303.15$ K	$T=289.15$ K	$T=303.15$ K
Only carrier fluid	1.65 [†]	2.76 [†]	3.36	3.62
C17 (10 wt.%)	3.07	3.39	4.13	4.57
RT21HC (10 wt.%)	3.08	3.27	4.04	4.62

[†] α_p , values for water were calculated from density data reported in Refprop 9.0 [50]

Density of nanoemulsions can be predicted by using the following equation based on mixing theory:

$$\frac{1}{\rho_{PCME}} = \frac{\varphi_{PCM}}{\rho_{PCM}} + \frac{\varphi_{SDS}}{\rho_{SDS}} + \frac{1 - \varphi_{PCM} - \varphi_{SDS}}{\rho_{CF}} \quad (5)$$

In Figure 13b densities experimentally measured for RT21HC–nanoemulsions at the two extreme temperatures (*i.e.* 288.15 K and 303.15 K) are compared with the values provided by Eq.(5), as an example. Measured and theoretical values compared quite well, with maximum deviations lower than 0.35%, validating the correctness of this equation for the prediction of the nanoemulsion density [84,85].

With the aim of deepening in the knowledge of specific molecular interactions existing in PCM emulsions, it may be useful to quantitative estimate excess thermodynamic functions such as excess molar volume, V_m^E [86]. Excess molar volume compares the volumetric behavior of a mixture with the ideal behavior, according to the following relation:

$$V_{m,PCME}^E = x_{PCM} \cdot M_{PCM} \left(\frac{1}{\rho_{PCME}} - \frac{1}{\rho_{PCM}} \right) + x_{CF} \cdot M_{CF} \left(\frac{1}{\rho_{PCME}} - \frac{1}{\rho_{CF}} \right) + x_{SDS} \cdot M_{SDS} \left(\frac{1}{\rho_{PCME}} - \frac{1}{\rho_{SDS}} \right) \quad (6)$$

Since we do not know the molecular mass of bulk–RT21HC nor the density of solid bulk–*n*–heptadecane, excess molar volumes were only calculated for C17–emulsions when PCM droplets were in liquid phase (see Figure 13c). Even in that last case, it must be pointed out that Eq.(6) does not represent in rigor an excess property since SDS (solid) is not in the same state as the PCM

droplets or carrier fluid (liquid) and, consequently, an ideal reference state cannot be defined. As it can be observed, both C17-in-water and C17-in-(ethylene glycol+water) emulsions exhibit slight contractive volumetric behaviors, more pronounced with increasing paraffin loading. In addition to a more efficient molecular packing, negative V_m^E values may suggest the existence of attractive interactions between the components.

4. Conclusions

Phase change material emulsions with fine paraffin drops were prepared by means of a solvent-assisted method. No evidence of phase separation in the nanoemulsions or significant growth in PCM drops was detected through time or when samples were subjected to freeze-thaw cycling or mechanical shear stress tests. Samples also proved to be resistant to several freeze-thaw cycles, even 9 months after preparation. The addition of small portion of ethylene glycol (20% in mass) to the carrier fluid did not alter the good stability of the samples, but provided good protection against carrier fluid freezing. DSC results showed that, while PCMEs exhibited melting transitions only $\sim 1\text{--}3$ K below those of bulk-PCMs, nanoemulsions presented strong sub-cooling effects of up to 13 K. Despite the multiple attempts to try to solve this problem by promoting heterogeneous nucleation in the PCM drops using different paraffinic nucleating agents, only partial reductions of sub-cooling effect (up to 3.2 K) were achieved with tested paraffins. The incorporation of a nucleating agent reduced the latent heat of the PCMEs, but the lower sub-cooling effect of these nanoemulsions led to slightly better ideal heat storage capacities. As expected, thermal conductivity decreased with increasing PCM loading. Reductions in this property reached the 9% for the highest dispersed phase contents. Decreases in density up to 3% were also observed as a consequence of paraffin dispersion. In addition, variations in density around the 1% were observed when PCM drops underwent the phase change. A deeper analysis of volumetric behavior showed contractive excess molar volumes which would suggest a more efficient molecular packing and/or the existence attractive interactions between the components of the emulsion. Finally, additional measurements of other transport properties such as the dynamic viscosity would complete the characterization of designed nanoemulsions and would contribute to a better understanding of these materials, not only as energy storage media but also as heat transfer fluids.

Acknowledgements

D.C. was recipient of a postdoctoral fellowship from Xunta de Galicia (Spain). M.A.M acknowledges a predoctoral contract within the Project ENE2014-55489-C2-2-R supported by Spanish Ministry of Economy and Competitiveness and EU FEDER Program. J.I.P. thanks a predoctoral fellowship from Xunta de Galicia.

Nomenclature

Latin symbols

$AAD\%$	Percentage absolute average deviations
c_p	Isobaric specific heat capacity [J/g K]
C17	<i>n</i> -heptadecane
C28	<i>n</i> -octacosane
CF	Carrier fluid
DSC	Differential scanning calorimeter
EG	Ethylene glycol
HVAC	Heating, ventilation and air conditioning
HTF	Heat transfer fluid
k	Thermal conductivity [W/mK]
M	Molar mass [g/mol]
NA	Nucleating agent
PCM	Phase change material
PCS	Phase changing slurry
PCME	Phase change material emulsion
pdl	Polydispersity index
RT55	Rubitherm RT55 paraffin wax
RT70HC	Rubitherm RT70HC paraffin wax
SDS	Sodium dodecyl sulfate
T	Temperature [K]
TES	Thermal energy storage
X	Mole fraction
V_m^E	Excess molar volume
W	Water

Greek and composite symbols

α_p	Isobaric thermal expansivity [K ⁻¹]
β	DSC scanning rate [K/min]
Δh	Enthalpy [J/g]
ϕ	Volume fraction
φ	Mass fraction
ρ	Density [g/cm ³]

Subscripts

α	Secondary thermal event
C	Crystalline phase
CF	Carrier fluid
L	Liquid
lat.	Latent
m	Melting
PCM	Phase change materials
PCME	Phase change material emulsion
peak	Thermal event peak
R	Rotator
S	Solid

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HIGHLIGHTS

- PCMEs with 2–10 wt.% of paraffin and droplet sizes of ~90–150 nm were designed
- Samples are stable over time, throughout freeze–thaw cycles and under stirring
- Enhancements in energy storage capacity may reach 26%
- Tested nucleating agents slightly reduced sub-cooling of PCMEs
- k and ρ decrease with PCM concentration up to 9% and 3%, respectively