MOBILIZED THERMAL ENERGY STORAGE FOR HEAT RECOVERY FOR DISTRIBUTED HEATING

Weilong Wang

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MOBILIZED THERMAL ENERGY STORAGE FOR HEAT RECOVERY FOR DISTRIBUTED HEATING

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Akademisk avhandling

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Abstract

Conventional energy sources—oil and electricity—dominate the heat supply market. Due to their rising costs and their negative environmental effects on global climate change, it is necessary to develop an alternative heat supply system featuring low cost, high energy efficiency and environment friendliness. At present, it is often challenging to supply heat to detached buildings due to low energy efficiency and high distribution cost. Meanwhile, significant amounts of industrial waste and excess heat are released into the environment without recycling due to the difficulty of matching time and space differences between suppliers and end users. Phase change materials (PCMs), with the advantages of being storable and transportable, offer a solution for delivering that excess heat from industrial plants to detached buildings in sparse, rural areas.

The objective of this thesis is to study PCMs and latent thermal energy storage (LTES) technology, and to develop a mobilized thermal energy storage (M-TES) system that can use industrial waste or excess heat for heat recovery and distribution to areas in need.

Organic PCMs were chosen for study because they are non-toxic and non-corrosive, and they exhibit no phase separation and little sub-cooling when compared to inorganic PCMs. Two major issues including leakage of liquid PCMs and low thermal conductivity. Polyethylene glycol (PEG) was chosen to help analyze the thermal behavior of organic PCMs and PEG-based form-stable composites. To overcome the issue of low thermal conductivity, modified aluminum nitride (AlN) powder was added to the composites. Increased thermal conductivity traded off decreased latent heat. The PEG/EG composite, prepared by mixing the melted PEG into an expanded graphite (EG) matrix showed good thermal performance due to its large enthalpy and high thermal conductivity.

To make a systematic study of the M-TES system, a compact lab-scale system was designed and built. Characteristics of PCM were studied, and the performance of the direct-contact TES container was investigated. A case study using an M-TES system to deliver heat from a combined heat and power (CHP) plant to a small village was conducted. A technical and economic feasibility study was conducted for an integrated heat supply system using the M-TES system. In addition, the options for charging a TES container at a CHP plant were analyzed and compared from the viewpoints of power output, heat output and incomes.
Abstract

Conventional energy sources—oil and electricity—dominate the heat supply market. Due to their rising costs and their negative environmental effects on global climate change, it is necessary to develop an alternative heat supply system featuring low cost, high energy efficiency and environment friendliness. At present, it is often challenging to supply heat to detached buildings due to low energy efficiency and high distribution cost. Meanwhile, significant amounts of industrial waste and excess heat are released into the environment without recycling due to the difficulty of matching time and space differences between suppliers and end users. Phase change materials (PCMs), with the advantages of being storable and transportable, offer a solution for delivering that excess heat from industrial plants to detached buildings in sparse, rural areas.

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Keywords: Mobilized thermal energy storage system; Phase change materials; Polyethylene glycol; Form-stable; Thermal conductivity; Industrial heat; Detached building; Sweden
Sammanfattning

Traditionell energi, olja och elektricitet, upptar det mesta av värmeförsörjningsmarknaden. På grund av ökande olje- och elektricitetskostnader och dessa energikällors möjliga negativa konsekvenser på den globala klimatförändringen är det nödvändigt att utveckla ett alternativt värmeförsörjningssystem, som har låg kostnade, hög energieffektivitet och som är miljövänligt. I det nuvarande värmeförsörjningssystemet är det dessutom svårt att försörja hus som ligger utanför fjärrvärmennätet på grund av värme- och elektricitetskostnader. Samtidigt släpps betydande mängder industriell spill- och överskottsvärme ut i miljö utan någon återvinning på grund av svårigheter att knyta ihop värmekällor med slutanvändare.

Fasomvandlingsmaterial (PCM) har fördelen att de kan förvaras och transporteras och erbjuder därmed en lösning till hur värme kan levereras med hög energidensitet från industriella anläggningar till glesbebyggda områden och byggnader som ej är anslutna till fjärrvärmennätet.

Målet med denna avhandling är att studera fasomvandlingsmaterial och teknik för latenta termiska energilager samt att utveckla sk. mobila termiska värmelager (M-TES) för att kunna återvinna industriell spill- och överskottsvärme, speciellt för leverans till oanslutna byggnader och glesbebyggda områden.

Organiska fasomvandlingsmaterial valdes ut för att studeras i denna avhandling på grund av att de, till skillnad mot icke-organiska, är giftfria, korrosionsfria, har ingen fasseparation och liten underkylning. Emellertid finns två betydande problem, läckage av flytande fasändringsmaterial och låg termisk konduktivitet. För att undvika läckage under fasomvandlingen valdes polyetylenlykol (PEG) ut för att studera det termiska beteendet hos organiskt fasändringsmaterial och PEG baserat stabila kompositer. För att överkomma problemet med låg termisk konduktivitet, blandades kompositerna med modifierat aluminiumnitridpulver. Tillsatsen av aluminiumnitridpulver gav ökad termisk konduktivitet men på bekostnad av den latenta värme kapaciteten. PEG/EG komposit, som tillverkats genom att hålla smått PEG i en matris av expanderad grafit (EG), visade i jämförelse med de två PEG materialen bättre termiska egenskaper på grund av det höga smältvärmet och den höga termisk ledningsförmåga.

För att göra en systematisk studie av M-TES systemet, designades och byggdes ett kompakt system i laboratorieskala för detta forskningsprojekt. Karakteristiken hos fasändringsmaterialet, studerade i den direktverkande värmeväxelaren studerades och prestanda vid laddning och urladdning undersöktes hos TES behållare, där de två medierna var i direkt kontakt med varandra. En fallstudie utfördes även för användning av M-TES systemet för att leverera värme från ett kraftvärmeverk till en liten by. Dessutom genomfördes en förstudie som inkluderade en teknisk och ekonomisk utvärdering av integrerade värmetillförselsystem. Utöver detta har även möjligheten att ladda TES behållare i kraftvärmeverket analyserats och jämförts med avseende på kraftproduktion, värme produktion och intäkt.

Nyckelord: mobil termiskt energilager; värmelagringssystem; polyetylenlykol; formstabil; termisk ledningsförmåga; industriell värme; oanslutna byggnader; Sverige
List of Papers

This thesis is based on the following papers, which are referred in the text by Roman numbers.


VI. Wang WL, Yan J, Dahlquist E. Thermal performance of the mobilized thermal energy storage system. Accepted by International Conference on Applied Energy, Perugia, Italy, May. 16-18th, 2011.

Other publications excluded in this thesis during the Ph.D study

Table of Contents

Abstract ............................................................................................................................................. I
Sammanfattning .............................................................................................................................. III
List of Papers ................................................................................................................................... V
List of Figures ................................................................................................................................. IX
List of Tables ................................................................................................................................... XI
Nomenclature and abbreviations .................................................................................................. XIII

1. Introduction .................................................................................................................................... 1
   1.1 Background ........................................................................................................................... 1
       1.1.1 Current status of energy consumption and heat supply in Sweden ..................... 1
       1.1.2 Advantages of TES technology for distributed heating .................................... 3
       1.1.3 State of the art on thermal energy storage materials and technology ............. 3
       1.1.4 State of the art on mobilized thermal energy system ....................................... 5
   1.2 Problems of delivering industrial heat to distributed users ........................................ 9
   1.3 Objectives of this work ...................................................................................................... 9
   1.4 Methods .......................................................................................................................... 10
   1.5 Thesis outline .................................................................................................................. 11

2. Design, modification and analysis of thermal energy storage materials ................................. 13
   2.1 Experiments .................................................................................................................... 13
       2.1.1 Materials and instruments ................................................................................... 13
       2.1.2 Preparation and modification of PCM ................................................................. 14
       2.1.3 Characterization .................................................................................................... 14
   2.2 Thermal performance of organic thermal energy storage materials ............................ 16
   2.3 Thermal properties of form-stable TES composites ................................................... 17
       2.3.1 Preparation of TES composites ........................................................................... 17
       2.3.2 Thermal property investigation ............................................................................ 18
   2.4 Enhanced thermal conductivity by AlN modification ..................................................... 23
       2.4.1 Preparation ........................................................................................................... 23
       2.4.2 Mechanism of modification on AlN ..................................................................... 23
       2.4.3 Performance of modification on AlN ................................................................. 25
       2.4.4 Thermal conductivity enhancement and analysis ............................................ 27
   2.5 Comparison of AlN-modified PEG/SiO₂ and PEG/EG ............................................... 28
   2.6 Summary ......................................................................................................................... 29
List of Figures

Figure 1.1 Use of Energy in Sweden 2008 (TWh) [1]..................................................................................... 1
Figure 1.2 Heat supply alternation for space heating and hot water in detached houses in Sweden 2008 (totally 31.8 TWh/y) [4].................................................................................................................. 2
Figure 1.3 Diagram of mobilized thermal energy storage system ................................................................... 5
Figure 1.4 Direct-contact TES container based M-TES system, TransHeat, Germany [77].......................... 6
Figure 1.5 Indirect-contact TES container based M-TES system, Alfred Schneider, Germany [74]............. 6
Figure 1.6 Thermal energy storage system developed by Climate Well [81]................................................ 7
Figure 1.7 Demonstration of the M-TES application at LSG Sky Chefs in Cologne [75]............................... 8
Figure 1.8 Diagram of main scientific work in this thesis .............................................................................. 11
Figure 2.1 Schematic diagram of the Hotdisk thermal conductivity instrument ........................................... 15
Figure 2.2 Experimental instruments for heat storage and release test........................................................ 16
Figure 2.3 DSC curves of various pure PEG during the heating process ..................................................... 16
Figure 2.4 DSC curves of various pure PEG with during the freezing process ............................................. 16
Figure 2.5 (a) Reaction instrument; (b) Vacuum dryer; (c) Shaping instrument; (d) Samples ....................... 18
Figure 2.6 DSC curves of PEG/SiO2 with different mass ratios during the heating process ....................... 19
Figure 2.7 DSC curves of PEG/SiO2 with different mass ratios during the freezing process ....................... 19
Figure 2.8 POM photos of pure PEG during the heating and freezing processes (X200): (a) 25° C (heating process), (b) 60° C (heating process), (c) 64° C (heating process), (d) 68° C (cooling process), (e) 54° C (cooling process) and (f) 25° C (cooling process) ........................................... 20
Figure 2.9 POM photos of pure PEG during the heating and freezing processes (X100): (a) 25° C (heating process), (b) 60° C (heating process), (c) 64° C (heating process), (d) 120° C (heating process), (e) 54° C (cooling process) and (f) 25° C (cooling process) .......................................................... 21
Figure 2.10 TG curves of pure PEG, SiO2 and composites ............................................................................ 22
Figure 2.11 DSC curves of the TES composites under thermal cycles .......................................................... 22
Figure 2.12 The structural formula of KH550 ............................................................................................... 24
Figure 2.13 Proposed schematic of modification mechanism for KH550: (a) Hydrolysis of KH550; (b) modification of AlN ........................................................................................................................................... 24
Figure 2.14 The structural formula of the NDZ-401 coupling agent ............................................................. 24
Figure 2.15 Proposed schematic of modification mechanism for NDZ-401 ................................................... 25
Figure 2.16 The photos of AlN aqueous suspension before and after modification ...................................... 25
Figure 2.17 Effect of agent amount on AlN modification: (a) KH550; (b) NDZ-401 ..................................... 26
Figure 2.18 Comparison of the PH values of modified AlN aqueous suspensions using various coupling agents ......................................................................................................................................... 27
Figure 2.20 Effect of added AlN amount on thermal conductivity ............................................................ 28
Figure 3.1 Setup of oil-bath based thermal test ............................................................................................. 31
Figure 3.2 Sketch of the direct-contact M-TES system ................................................................................ 32
Figure 3.3 Photos of the experimental facility built at MdH ........................................................................ 33
Figure 3.4 Tests of repeated heat storage and release cycles ...................................................................... 34
Figure 4.1 Location of heat supplier and end-user ...................................................................................... 39
Figure 4.2 Scheme of the existing and modified heat supply system in Ärla .............................................. 40
Figure 4.3 Scheme of the integrated CHP plant and M-TES system .......................................................... 43
Figure 4.4 Effect of steam-extracting options on the CHP plant including: (a) power output, (b) heat output, (c) steam-extracting flow rate and (d) income of electricity and heat production............. 44
List of Tables

Table 1.1 Energy density comparison of hot water and PCMs ................................................................. 3
Table 1.2 Comparison of organic and inorganic PCMs [13, 15, 20, 24-26] .............................................. 4
Table 1.3 Demonstrations of the M-TES system in Japan [82] ................................................................. 9
Table 2.1 Characteristics of the experimental materials .......................................................................... 13
Table 2.2 Information of the experimental instruments and testing devices .......................................... 14
Table 2.3 Measured thermal properties of pure PEG with different molecular weights ....................... 17
Table 2.4 Measured thermal properties of the composite materials ....................................................... 19
Table 2.5 Measured thermal properties of the composite materials under thermal cycles ................. 23
Table 2.6 Comparison of modified PEG/SiO₂ (AlN=15wt. %) and PEG/EG composites ...................... 28
Table 3.1 Comparison of the charging processes at different flow rates of oil ..................................... 35
Table 3.2 Comparison of the discharging processes at different flow rates of oil ............................... 36
Table 4.1 Local heat supply with different scenarios .......................................................................... 42
Table 4.2 Description of the four options for heating the TES container .......................................... 42
**Nomenclature and abbreviations**

**Nomenclature:**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_p$</td>
<td>specific heat (kJ/kg °C)</td>
</tr>
<tr>
<td>$\Delta H_m$</td>
<td>latent heat of fusion (kJ/kg)</td>
</tr>
<tr>
<td>$\Delta H_f$</td>
<td>latent heat of freezing (kJ/kg)</td>
</tr>
<tr>
<td>$M$</td>
<td>quantity of the materials (kg)</td>
</tr>
<tr>
<td>$T_m$</td>
<td>melting temperature (°C)</td>
</tr>
<tr>
<td>$T_f$</td>
<td>freezing temperature (°C)</td>
</tr>
<tr>
<td>$Q$</td>
<td>total heat capacity of a lorry (MWh)</td>
</tr>
<tr>
<td>$C_p$</td>
<td>specific heat (kJ/kg °C)</td>
</tr>
<tr>
<td>$Q_{m}$</td>
<td>enthalpy (kJ/kg)</td>
</tr>
<tr>
<td>$T_i$</td>
<td>initial temperature (°C)</td>
</tr>
<tr>
<td>$T_f$</td>
<td>maximum temperature (°C)</td>
</tr>
<tr>
<td>$\rho$</td>
<td>density (kg/m³)</td>
</tr>
<tr>
<td>$R_n$</td>
<td>revenue of period n (€)</td>
</tr>
<tr>
<td>$C_n$</td>
<td>cost of period n (€)</td>
</tr>
<tr>
<td>$n$</td>
<td>year</td>
</tr>
<tr>
<td>$I_o$</td>
<td>initial investment (€)</td>
</tr>
<tr>
<td>$i$</td>
<td>discount rate</td>
</tr>
<tr>
<td>$Q_{oil,in}$</td>
<td>energy of inlet oil (kWh)</td>
</tr>
<tr>
<td>$Q_{oil,out}$</td>
<td>energy of outlet oil (kWh)</td>
</tr>
<tr>
<td>$Q_{s,pcm}$</td>
<td>sensible energy of PCM (kWh)</td>
</tr>
<tr>
<td>$Q_{l,pcm}$</td>
<td>latent energy of PCM (kWh)</td>
</tr>
<tr>
<td>$Q_{oil,cont}$</td>
<td>energy of oil in the container (kWh)</td>
</tr>
<tr>
<td>$Q_{loss}$</td>
<td>energy loss (kWh)</td>
</tr>
<tr>
<td>$M_{oil}$</td>
<td>quality of oil (kg)</td>
</tr>
<tr>
<td>$C_{poil}$</td>
<td>specific heat of oil (kJ/kg °C)</td>
</tr>
<tr>
<td>$T_{oil,in}$</td>
<td>temperature of inlet (°C)</td>
</tr>
<tr>
<td>$T_{oil,out}$</td>
<td>temperature of outlet (°C)</td>
</tr>
<tr>
<td>$K_i$</td>
<td>thermal conductivity (W/m °C)</td>
</tr>
<tr>
<td>$S_{cont}$</td>
<td>areas of surface of the container (m²)</td>
</tr>
<tr>
<td>$T_{wall}$</td>
<td>temperature of the container wall (°C)</td>
</tr>
<tr>
<td>$T_{room}$</td>
<td>room temperature (°C)</td>
</tr>
<tr>
<td>$T_{ins}$</td>
<td>thickness of the insulation (m)</td>
</tr>
</tbody>
</table>

**Abbreviations:**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlN</td>
<td>Aluminum nitride</td>
</tr>
<tr>
<td>CHP</td>
<td>Combined heat and power</td>
</tr>
<tr>
<td>DH</td>
<td>District heating</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimeter</td>
</tr>
<tr>
<td>EEM</td>
<td>Eskilstuna Energi och Miljö AB</td>
</tr>
<tr>
<td>EG</td>
<td>Expanded graphite</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>FT-IR</td>
<td>Fourier transformation infrared spectroscope</td>
</tr>
<tr>
<td>HTO</td>
<td>Heat transfer oil</td>
</tr>
<tr>
<td>IRR</td>
<td>Internal rate of return</td>
</tr>
<tr>
<td>LTES</td>
<td>Latent thermal energy storage</td>
</tr>
<tr>
<td>M-TES</td>
<td>Mobilized thermal energy storage</td>
</tr>
<tr>
<td>NPV</td>
<td>Net present value</td>
</tr>
<tr>
<td>PCMs</td>
<td>Phase change materials</td>
</tr>
<tr>
<td>PEG</td>
<td>Polyethylene glycol</td>
</tr>
<tr>
<td>pH</td>
<td>Pondus hydrogenii</td>
</tr>
<tr>
<td>POM</td>
<td>Polarizing optical microscope</td>
</tr>
<tr>
<td>PP</td>
<td>Payback period</td>
</tr>
<tr>
<td>POM</td>
<td>Polarizing optical microscope</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electronic microscope</td>
</tr>
<tr>
<td>SES</td>
<td>Sensible energy storage</td>
</tr>
<tr>
<td>SG</td>
<td>Silica gel</td>
</tr>
<tr>
<td>SiO₂</td>
<td>Silicon dioxide</td>
</tr>
<tr>
<td>TES</td>
<td>Thermal energy storage</td>
</tr>
<tr>
<td>TMA</td>
<td>Thermal Mechanism Analysis</td>
</tr>
<tr>
<td>TG</td>
<td>Thermogravimetric analyzer</td>
</tr>
<tr>
<td>TPS</td>
<td>Transient plane source</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray single crystal diffraction</td>
</tr>
</tbody>
</table>
1. Introduction

1.1 Background

1.1.1 Current status of energy consumption and heat supply in Sweden

- Energy use in Sweden

In 2008, total energy use in Sweden amounted to 612 TWh. Of this, total final energy use across three critical sectors made up 397 TWh (Figure 1.1), a 34% increase since 1970 [1].

![Figure 1.1 Use of energy in Sweden 2008 (TWh) [1]](image)

In the residential and service sector, energy use reached 141 TWh, accounting for 36% of the total final energy use. Electricity and district heating are the primary energy consumers in this sector. More than half their supply—78.2 TWh—was consumed for space heating and domestic hot water usage in 2008 [2]. Of this, 31.8 TWh (41%) were used in detached buildings, 25.2 TWh (32%) in multi-dwelling buildings, and 21.2 TWh (27%) in nonresidential buildings. Energy use in the industry sector accounted for 151 TWh, about 38% of the final energy use. The main energy carriers in industry are electricity (35%) and biofuels (37%), complemented by energy from fossil sources (25%). [Fossil energy was provided by 16 TWh of oil products, 16.4 TWh of coal and coke, and 5.4 TWh of natural gas.][1]

- Heat supply in detached buildings and sparse areas in Sweden

In Sweden, the number of detached and multi-unit dwellings in the country is steadily increasing. In
In 2008, there were about 4.5 million dwellings, 40% more than in 1970. More than half the Swedish population (56%) lives in detached houses [1]. As of 2007, there were 1.74 million detached houses in use, of which 183,000 were located in farmlands. One third of these were built between 1941 and 1970, and another third between 1971 and 1990. Those built during the early stage are typically equipped with a boiler heating system located in the basement. The houses built later are mostly heated with electricity, either directly with resistance heaters or with an electrical boiler heating system; these houses usually have no basement, boiler room, or chimney [3].

![Figure 1.2 Heat supply alternation for space heating and hot water in detached houses in Sweden 2008 (totally 31.8 TWh/y) [4]](image)

Figure 1.2 shows that about 10% of the detached buildings were heated by district heating, 15% were heated by biofuels, and 14% were heated by oil. Electricity represents 13% of the total heat supply exclusively, and 21% when combined with other sources. The most common way of heating in detached houses is with electric heating. Of these dwellings, over half have direct electric heating, and the rest use waterborne electric heating. The main reasons for the high proportion of electric heating are that it is cheap to install and simple to operate. In 2007, the total use of electricity for space heating and domestic hot water production in detached houses was 13.7 TWh.

Although the price of electricity in Sweden has historically been low compared to other European countries, it is gradually approaching the European level. Moreover, high electricity consumption increases the production demand on Sweden’s power plants, especially during the high peak load in the cold winter. Finally, Figure 1.2 also indicates that oil shares 14% of the total heat need of detached buildings. The high price of oil and pollution from the oil combustion are pushing people to search for a clean, sustainable heat supply technology. At present, the Swedish government is promoting a subsidy program for the conversion of electric and oil heating systems. All these factors indicate that there is a huge potential for the conversion of the existing heating system.
1. Introduction

1.1.2 Advantages of TES technology for distributed heating

According to the reports on Swedish energy consumption, residential heat demand accounts for a large portion of the total heat consumption, including space heating and hot tap water usage, especially during winter. In the population-dense regions, heat is delivered efficiently by the district heating (DH) network, connecting to centre heating systems or combined heat and power (CHP) plants. However, plenty of detached buildings such as schools and office buildings as well as sparse areas with only a couple of houses are not connected to the DH system. Heat demand for these is usually covered by small-scale heaters such as pellet or electrical boilers, or by a small local heat supply centres usually consisting of biomass or fossil fuel boilers. Fossil fuel is quite costly and produces greenhouse gases (GHGs), specifically carbon dioxide emissions. Meanwhile, abundant waste or excess heat is produced by industrial plants, which creates potential for the recovery of that lost industrial heat. Clearly, it would be of significant importance to find a feasible and economic way to transport the excess industrial heat to detached buildings and sparse areas.

There are two options for transporting industrial heat to end users. One is to build a new pipe network connecting plants and users; this has been discussed and the concerns mainly focus on decreasing the investment cost of the infrastructure construction [5-12]. However, given the small heat demand of distributed users, this method is not economically feasible. The second is to transport heat using a tank filled with hot water or phase change materials (PCMs). Table 1.1 indicates that energy density plays a key role in heat transportation. Hot water has a low energy density and a high transport cost, and hence it is only suitable for transport across a short distance. By comparison, PCMs have large energy densities because they take advantage of additional latent heat during the phase transition. Thus PCMs offer a solution for delivering heat economically over a long distance between the industrial plants and the end users.

Table 1.1 Energy density comparison of hot water and PCMs

<table>
<thead>
<tr>
<th>Storage materials</th>
<th>Energy density (50-100 °C)</th>
<th>Cost of transportation (26 tone/lorry, 10km distance)</th>
<th>Distance (26 tone/lorry)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hot water</td>
<td>50</td>
<td>3.9 Euro cent/kWh</td>
<td>15 km</td>
</tr>
<tr>
<td>PCMs</td>
<td>100~130</td>
<td>1.4~1.9 Euro cent/kWh</td>
<td>30 km</td>
</tr>
</tbody>
</table>

*1 Euro = 10.491 Kr

1.1.3 State of the art on thermal energy storage materials and technology

Latent thermal energy storage (TES) is attractive due to its large energy storage density and its ability to store and release heat at a constant temperature corresponding to the phase change temperature. PCMs can be grouped as inorganic and organic compounds. Inorganic compounds include salt hydrates, salts metals and alloys, etc., while organic compounds consist of paraffin, non-paraffin, fatty acids, etc. [13-17].
The prospective energy storage materials should have the following characters for actual application [17, 18]:

- large latent heat and high thermal conductivities;
- variable operation temperatures to accommodate different practical applications;
- thermal stability for a long-term use;
- non-toxic, non-corrosive and non-explosive qualities;
- low prices and large availability.

A comparison of organic and inorganic materials can be seen in Table 1.2. Most organic PCMs are non-corrosive, thermal stable, exhibit little or no sub-cooling and are compatible with most building materials, in addition to having a high latent heat per unit weight with low vapor pressure. Their disadvantages are low thermal conductivity, high changes in volume on phase change, and flammability. Inorganic materials have a high latent heat per unit volume and high thermal conductivity, and they are non-flammable and low cost compared to organics. However, they are corrosive to most metals and suffer from decomposition and serious sub-cooling, which can affect their phase change properties. The applications of inorganic PCMs require the use of nucleating and thickening agents to minimize sub-cooling and phase separation [19-23].

Table 1.2 Comparison of organic and inorganic PCMs [13, 15, 20, 24-26]

<table>
<thead>
<tr>
<th></th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic</td>
<td><img src="image1" alt="Organic PCMs" /></td>
<td><img src="image2" alt="Disadvantages of Organic PCMs" /></td>
</tr>
<tr>
<td></td>
<td>● No corrosives</td>
<td>● Lower phase change enthalpy</td>
</tr>
<tr>
<td></td>
<td>● Low or none sub-cooling</td>
<td>● Low thermal conductivity</td>
</tr>
<tr>
<td></td>
<td>● Chemical and thermal stability</td>
<td>● Flammability</td>
</tr>
<tr>
<td></td>
<td>● Volume change</td>
<td></td>
</tr>
<tr>
<td>Inorganic</td>
<td><img src="image3" alt="Inorganic PCMs" /></td>
<td><img src="image4" alt="Disadvantages of Inorganic PCMs" /></td>
</tr>
<tr>
<td></td>
<td>● Greater phase change enthalpy</td>
<td>● Sub-cooling</td>
</tr>
<tr>
<td></td>
<td>● High heat transfer rate</td>
<td>● Corrosion</td>
</tr>
<tr>
<td></td>
<td>● Inflammability</td>
<td>● Phase separation</td>
</tr>
<tr>
<td></td>
<td></td>
<td>● Lack of thermal stability</td>
</tr>
</tbody>
</table>

The significant TES applications can be divided into two groups: heat and cool thermal storage. These include solar energy storage [27-32], power peak shift [33-38], food and medicine protection and preservation [39-42], passive energy storage in architecture [43-48], electric device cooling [49-52], thermal cooling supply [53-55], etc. Until now, most work has focused on the development of new TES materials and composites as well as heat transfer enhancement in application. A form-stable composite has been developed without any leakage and volume change during the phase transition, which extends the use of PCMs for specific applications and simultaneously decreases the cost for encapsulation of the transport vessel [26, 56-63].
enhancement of heat transfer in PCM applications is of significance regarding the thermal conductivity of PCMs and the design structure of TES facilities [64-73].

1.1.4 State of the art on mobilized thermal energy system

- Concept of the M-TES system

The mobilized thermal energy storage (M-TES) system, illustrated in Figure 1.3, is an energy transportation method using high energy-dense technology. This system has the potential to meet the heating demand of detached buildings and sparse areas, including use in combination with other heat supply systems, and can reduce greenhouse gas emissions by replacing fossil-based heat sources in addition to saving high-grade electricity energy. The M-TES system consists of a thermal energy storage container, a heat exchanger for charging and discharging stations, a pump and a lorry. In it, TES materials play a key role in storing and releasing heat during the charging and discharging processes. A heat transfer oil (HTO) or water serves as a heat transfer medium for transferring heat from heat sources to end users [74-80].

![Figure 1.3 Diagram of mobilized thermal energy storage system](image)

Two types of TES containers have been designed based on different heat transfer mechanisms. One is the direct-contact TES container, in which TES material is mixed directly with a heat transfer medium. Hence, the PCM is required to be non-soluble in the transfer medium, and a large density difference between them is necessary to separate them from each other. In Germany, the TransHeat Company uses a direct-contact TES container (Figure 1.4). A heat transfer medium is pumped into the TES container through pipes to heat and melt the PCMs. In this dynamic charging process, direct contact between the PCMs and the transfer media results in a strong heat transfer performance. The thermal storage system has both sensible heat of the PCMs and the transfer media as well as the latent heat of the PCM. Finally, the heat transfer medium rises from the top pipes due to the density difference. The second type of containers is the indirect-contact TES container. It has an immersed heat exchanger, where heat transfer medium passes through the...
pipe’s interior and transfers heat to the TES materials. In this way, the heat transfer rate depends on the contact surface areas and the thermal conductivity of the PCM. In contrast, the direct-contact TES container has a higher heat transfer rate than the indirect-contact unit. Larger heat transfer rate could be gained by immersed heat exchanger design and modification of PCM. Figure 1.5 shows the TES container developed by the Alfred Schneider Company (also in Germany).

![Latentwärmespeicher Prinzip](image)

Figure 1.4 Direct-contact TES container based M-TES system, TransHeat, Germany [77]

![Indirect-contact TES container based M-TES system, Alfred Schneider, Germany](image)

Figure 1.5 Indirect-contact TES container based M-TES system, Alfred Schneider, Germany [74]

- Research and applications on M-TES system

In Sweden, Climate Well has developed a direct-contact TES system (Figure 1.6). Two storage tanks contain salt hydrate (thermal energy storage material) and water, separately. Both tanks are connected to each other by a pipe on the top. In the charging process, salt hydrate is heated and crystal water is released and evaporates, moving to the water tank. Thus, heat is stored in the salt container. In the discharging process, water evaporates from the water tank and is absorbed in the
salt tank. Heat can be released by recombining salt and crystal water. Moreover, to improve the performance of this system, air is extracted from the tank, reportedly increasing the water transport speed [81].

Figure 1.6 Thermal energy storage system developed by Climate Well [81]

In Germany, TransHeat Company uses a commercial M-TES system which is characterized by the direct-contact heat transfer technique. Two inorganic materials have been selected and developed as potential TES material candidates for different users; these are barium hydroxide (BaH₂O₂·8H₂O) and sodium acetate trihydrate (CH₃COONa·3H₂O). Another M-TES system is used by the Alfred Schneider Company, whose TES container is designed with immersed heat exchanger. At present, there is no report available about the practical applications or demonstrations for this type of M-TES system. However, in Japan, some institutes are also working in this field and have developed a container based on a prototype of TransHeat’s technique[76].

The earliest practical application of these systems was reported to be implemented in Germany. LSG Sky Chefs (Neu-Isenberg) must be recognized for its efforts to introduce innovative technology related to environment protection, and TransHeat contributed technique design and support for this effort [75]. The waste heat came from a power station, where generated process heat needed to be cooled down. Barium hydroxide was used as the energy storage medium. A truck provided 25 m³ of materials storing heat to LSG, and one container was found to store 4 MWh of heat—equal to 450 l of heating oil. At LSG, the water was used in kitchens and dishwashing facilities.
Another case in Germany involved the transport of heat to a school over a 10-km distance from a biomass power plant. The heat demand was approximately 1850 MWh per year, covered by a local oil boiler with an efficiency of 85%. In the modification of the existing system, transported heat became responsible for the base load heat demand, and the oil boiler was left as a backup for the peak demand. The heat transport technology was also from TransHeat, and sodium acetate trihydrate served as the storage material [76].

Three M-TES demonstrations have been implemented in Japan (Table 1.3). In Demonstration I, heat was delivered over 20 km between two factories. The purpose was to preheat feed water for a boiler in another factory, decreasing energy consumption and cost. Meanwhile, the heat was derived from (free) excess heat generated by an electric company, which decreased the operating cost to make it more economical and feasible. In Demonstrations II and III, the M-TES system supplied higher temperature heat, which can be used widely among residential or industrial end users. Moreover, it also can be used to drive absorption chillers to supply absorption cooling; this means that the M-TES system has significant potential in the heating and cooling supply market [82].

Figure 1.7 Demonstration of the M-TES application at LSG Sky Chefs in Cologne [75]
Table 1.3 Demonstrations of the M-TES system in Japan [82]

<table>
<thead>
<tr>
<th>Descriptions</th>
<th>Demonstration I</th>
<th>Demonstration II</th>
<th>Demonstration III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat source</td>
<td>Factory of SANYO Electric Co. Ltd. in Gunma</td>
<td>Sewage plant in Kiyose-city Tokyo</td>
<td>Kagaya factory of KURIMOTO, LTD in Osaka city</td>
</tr>
<tr>
<td>End user</td>
<td>Factory of Furukawa Sky Aluminum Corp. in Saitama</td>
<td>Civic gymnasium</td>
<td>Sumiyoshi factory</td>
</tr>
<tr>
<td>Distance</td>
<td>20 km</td>
<td>2.5 km</td>
<td>3 km</td>
</tr>
<tr>
<td>Usage</td>
<td>Preheat feeding water to a boiler</td>
<td>Supply of hot water to the absorption chiller generating cool water to air condition</td>
<td>Heat water for the bath of employees</td>
</tr>
<tr>
<td>Heat type</td>
<td>Excess steam heat</td>
<td>Waste gas form sludge incinerator</td>
<td>Waste gas from annealing furnace</td>
</tr>
<tr>
<td>Other info.</td>
<td>N.A.</td>
<td>N.A.</td>
<td>Container is a small one with 5 m³ and the storage capacity is about 415kWh</td>
</tr>
</tbody>
</table>

1.2 Problems of delivering industrial heat to distributed users

To transport industrial heat to distributed users, an effective system with a high heat density should be developed—one which is also simple to build and easy to run. It is not economically feasible to transport hot water by building a pipe network. It is not possible to transport hot water by a lorry over a long distance due to its low heat density. Because PCM-based LTES materials have large heat densities, usually 2 or 3 times that of the sensible heat of water, the M-TES system has been based on TES technology for heat transportation. In the M-TES system, TES materials and the structure of storage containers play a key role in the performance of the system. Meanwhile, inorganic materials used in the current M-TES system are not promising due to their low thermal stability caused by severe sub-cooling and phase separation; furthermore, they are also toxic and corrosive, resulting in strict requirements on container capsulation and fabrication materials. It may be instructive to develop M-TES system using organic PCMs. However, they have low thermal conductivities, especially when used in the indirect-contact TES containers, resulting in low heat transfer rates. The problems can be resolved from two aspects. One is to develop a new type of TES material with a large heat density and high thermal conductivity. The other is to develop direct-contact TES containers using organic materials. Thermal behavior and the performance of direct-contact TES containers during the charging and discharging processes require more investigation.

1.3 Objectives of this work

The objective of this thesis is to develop an LTES-based M-TES system to transport industrial
Mobilized thermal energy storage for heat recovery for distributed heating

waste or excess heat for use in distributed heating. This work has three goals: (1) design and investigate new form-stable TES composites for thermal conductivity enhancement, and find new suitable types of composites for indirect-contact containers; (2) investigate the thermal behavior and performance of direct-contact TES containers based on our newly designed and built lab-scale M-TES system; and (3) conduct and analyze a technical and economic feasibility study to evaluate the M-TES system. In addition, the heat charging options and the effect of the steam-extracting on the CHP plant are discussed in this work.

1.4 Methods

An analysis of both the existing heat supply systems for detached houses/sparse areas and thermal energy storage technology was the starting point for this study. Based on a survey of current heat supply measures and previous work, it was decided to develop a new heat transport system using PCM-based LTES technology to deliver industrial heat to end users.

Thermal energy storage technology plays a key role in the transport system, and hence the thermophysical properties of various phase change materials were studied to determine their potential; these included the phase transition melting and freezing temperatures, the latent heat capacity, the thermal stability, and phase change behaviors. On the basis of knowledge about PCM materials, the new form-stable PEG-based TES composites were prepared using different mechanisms and methods. Investigation of the properties of PCM materials and composites included the use of a scanning electronic microscope (SEM), a Fourier transformation infrared spectroscope (FTIR), a polarizing optical microscope (POM) and dynamic mechanic analysis (DMA). In addition, thermal conductivity enhancement was investigated because of the low thermal conductivities of organic PCM materials. Two methods were used, mixing high thermal conductivity additives and absorbing PCMs in the high thermal conductivity matrix.

Based on the existing heat supply for detached houses, a mobilized thermal energy storage (M-TES) system was developed using TES technology. A lab-scale of the M-TES system was designed, built and tested. In the experiments, the phase change behavior of the PCM materials was observed. Measurements were made of different flow rates of oil in the charging and discharging processes.

Simultaneously, a case study in Ärla, a small region in the Eskilstuna municipality in Sweden, was conducted using this new concept. In it, the combination of the M-TES and a locally existing pellet boiler system were used to replace an oil boiler system. A technical analysis was made to investigate the operating conditions of the modified heat supply system. The heat source of the combined heat and power plant and the different methods of extracting heat from the steam cycle in the power plant were studied via simulation using ASPEN software. The M-TES system was analyzed with respect to investment and operation cost. The existing and modified systems were compared in regard to cost distribution and relative heat cost. An economic analysis of the modified heat supply system was evaluated. Finally, a sensitivity study was conducted to investigate the impact of different parameters on the economic feasibility of the modified heat supply system.
1. Introduction

1.5 Thesis outline

This thesis is composed of three main parts, combining several research papers. Papers I, II, and III focus on the preparation and investigation of the new form-stable composites with high thermal conductivity. In Paper VI, the M-TES system was studied experimentally on the performance of lab-scale facility. In Papers IV and V, the feasibility of M-TES system for a modified heat supply is discussed. The outline of this thesis is as follows:

Chapter 1: Present the background of this thesis, including data on heat consumption in Sweden, the state-of-the-art of TES materials and technology, and the M-TES system. Propose problems in this research field and determine the objective of this thesis is to fix these problems scientifically.

Chapter 2: Present the preparation and investigation of two form-stable composites.

Chapter 3: Present the experiments of the lab-scale M-TES system and the investigation of the thermal behavior and performance of the direct-contact TES container.
Chapter 4: Provide a feasibility analysis based on a case study of the M-TES system for the modified heat supply.

Chapter 5: Draw conclusions.

Chapter 6: Propose future work for further development of the M-TES system.
2. Design, modification and analysis of thermal energy storage materials

Due to a low heat transfer rate in indirect-contact TES containers, TES materials need to be modified for improved thermal conductivities with reasonable thermal enthalpy. In this chapter, TES composites were prepared and studied to develop a new type of composite that can be used in an indirect-contact container. This chapter is based on Papers I, II and III.

2.1 Experiments

2.1.1 Materials and instruments

The materials and instruments used in the following experiments are described in Tables 2.1 and 2.2. Polyethylene glycol (PEG) is a substance having many applications in industrial manufacturing and in the field of medicine. PEG is prepared by polymerization of ethylene oxide. It is commercially available at different melting temperatures corresponding to a wide range of molecular weights. For this experiment, PEG (molecular weight from 800 to 10,000) was selected. The structure of PEG is HO-CH₂-(CH₂-O-CH₂)ₙ-CH₂-OH. Silica gel and expandable graphite are also commercially available. They are used as the supporting material and matrix in the composites, respectively. β-Aluminum nitride (β-AlN) is a commercial grade element that was selected to enhance thermal conductivity of TES composites; it was first modified by a commercial coupling agent composed of silane (KH550) and titanic acid ester (NDZ-401). Thus, all the materials and agents needed are available in the commercial market, which keeps the cost of material production low both now and in the future. All the instruments and measurement devices in Table 2.2 are available in the laboratory and testing centre.

Table 2.1 Characteristics of the experimental materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Abbreviation</th>
<th>Grade</th>
<th>Producers &amp; Suppliers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene glycol (molecular weight 800-10000)</td>
<td>PEG</td>
<td>R</td>
<td>Guangzhou Guanghua Co., Ltd., China</td>
</tr>
<tr>
<td>Silica gel</td>
<td>SG</td>
<td>I</td>
<td>Guangzhou Dongfeng Co., Ltd., China</td>
</tr>
<tr>
<td>β-Aluminum nitride</td>
<td>β-AlN</td>
<td>R</td>
<td>Foshan Jingshi CO., Ltd., China</td>
</tr>
<tr>
<td>Silane (coupling agent)</td>
<td>KH550</td>
<td>R</td>
<td>Dongguan Dongjia Co., Ltd., China</td>
</tr>
<tr>
<td>Titanic acid ester (coupling agent)</td>
<td>NDZ-401</td>
<td>R</td>
<td>Guangzhou Youyu Co., Ltd., China</td>
</tr>
<tr>
<td>Parting agent</td>
<td>770-NL</td>
<td>R</td>
<td>Loctite Company, America</td>
</tr>
<tr>
<td>Expandable graphite</td>
<td></td>
<td>I</td>
<td>Shanghai graphite CO., LTD.</td>
</tr>
</tbody>
</table>
Table 2.2 Information of the experimental instruments and testing devices

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Producer and Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Digital water-bath (HH-8)</td>
<td>Jintan Fuhua Instrument Co., Ltd., China</td>
</tr>
<tr>
<td>Digital motor stirrer (JB 90−S)</td>
<td>Biao Ben Model Company, China</td>
</tr>
<tr>
<td>Sartorius electro-scale</td>
<td>Sartorius Company, China</td>
</tr>
<tr>
<td>Vacuum dryer ( ZKF035)</td>
<td>Shanghai Laboratory Instrument works Co., Ltd.</td>
</tr>
<tr>
<td>Vacuum pump (2XZ-4)</td>
<td>Shanghai Deying Instrument Co., Ltd., China</td>
</tr>
<tr>
<td>DHX-9073B dryer</td>
<td>Shanghai Fuma Instrument Co., Ltd., China</td>
</tr>
<tr>
<td>Mould</td>
<td>Guangzhou Optical-mechanical-electrical Institute, China</td>
</tr>
<tr>
<td>Thermal analyzer (STA449C)</td>
<td>NETZSCH Company, Germany</td>
</tr>
<tr>
<td>Fourier transformation infrared spectroscope</td>
<td>Bruker Company, Germany</td>
</tr>
<tr>
<td>Scanning electronic microscope (XL-30)</td>
<td>Philips Company, Netherlands</td>
</tr>
<tr>
<td>Polarizing optical microscope (Axiolab)</td>
<td>ZEISS Company, Germany</td>
</tr>
<tr>
<td>Thermal Mechanism Analysis System (Instrument 2980)</td>
<td>TA Company, America</td>
</tr>
<tr>
<td>X-ray single crystal diffractometer (D/max-III A)</td>
<td>Rigaku Company, Japan</td>
</tr>
<tr>
<td>Hotdisk thermal analyzer (2500)</td>
<td>Hotdisk AB, Sweden</td>
</tr>
</tbody>
</table>

2.1.2 Preparation and modification of PCM

PEG was selected for study as an organic PCM. First, PEG/SiO₂ was prepared by blending PEG in silica gel solution. Second, AlN was added into the PEG/SiO₂ composites to enhance thermal conductivity. Third, another PEG/EG composite was prepared by mixing melted PEG with EG. The detailed preparation and conditions can be found in attached papers.

2.1.3 Characterization

- Scanning electronic microscopy (SEM)

The surface morphology of each sample was examined using a scanning electron microscope (Philips Scanning Electron Microscope XL30FEG). Microphotographs were taken of the surface made by fracturing the specimen in liquid nitrogen and then casting it with gold (AU) powder.

- Differential scanning calorimetry (DSC)

The melting point and the heat of fusion of the solid composite were determined using a differential scanning calorimeter calibrated with an indium standard in the range from -20 °C to 120 °C. The scanning rate was 10° C/min. The temperature accuracy was ±0.01 °C, and heat flow repeatability was 0.2 μW. The sample (10mg) was sealed in an aluminum pan. The melting and crystallization points were taken as onset temperatures. The latent heat of the PCM was determined by numerical integration of the peak thermal transition area. All DSC measurements were repeated two times for each sample.
Fourier transformation infrared spectroscope (FT-IR)

Fourier transformation infrared spectrum analysis was used to study the functional groups of PCM molecules. In this test, the PCM was melted and formed into a thin film on the surface of a KBr slice, which was used to conduct the FTIR tests.

Polarizing optical microscopy (POM)

An observation with a polarizing optical microscope was performed on a 12pol microscope equipped with a digital camera. The sample was placed between a microscope glass and a cover slip.

Thermal mechanism analysis system (TMA)

The physical characteristics of the materials were measured using a thermal mechanism analyzer (Instrument 2980, TA). Thermal elongation, expansion, and penetration during the thermal mechanism test applied a constant force at different temperatures and stretching ratios. A constant force of 1 N was applied at a constant heating rate of 5° C/min, with a nitrogen flow rate of 100ml/min, from -30° C to 130° C.

X-ray single crystal diffraction (XRD)

Samples were spotted with gold to prevent charging. X-ray diffraction was used to investigate the crystalline phase of the composite PCM powders, and XRD patterns of the composite PCMs were recorded in the 2θ range from 5° to 45°. XRD patterns were obtained by means of continuous scanning mode at the rate of 4°/min and operating conditions of 40kv and 100mA.

Thermogravimetric analyzer (TG)

The thermal stabilities of the materials were evaluated using a thermogravimetric analyzer (NETZSCH STA 449C) under a N2 atmosphere, and the scanning rate was 10° C/min in the temperature range of 25° C to 700° C.

Thermal conductivity analyzer

The thermal conductivity of the sample was measured by using the transient plane source (TPS) technique at room temperature. Figure 2.1 shows the schematic diagram of the Hotdisk thermal conductivity instrument. The sensor needs to be placed between two identical samples. The samples should be tightened for good contact with the sensor.

Figure 2.1 Schematic diagram of the Hotdisk thermal conductivity instrument

Experiments on heat storage and release performance
Figure 2.2 shows the experimental instrument for the heat storage and release test. Phase change material and the composites were put into two identical tubes. One thermocouple was placed in the middle of each tube. First, the two test tubes were put in the water at room temperature. Next, the two tubes were put into a water bath at the constant temperature. After the sample reached the designed temperature, the two tubes were put into the water at the same temperature again. The temperature measured by the thermocouple was recorded automatically using an Agilent data acquisition instrument.

![Experimental instruments for heat storage and release test](image)

2.2 Thermal performance of organic thermal energy storage materials

First, thermal properties of PEG were measured by DSC calorimetry. The DSC curves for PEG are illustrated in Figures 2.3 and 2.4, respectively, and the detailed thermal properties are also presented in Table 2.3.

![DSC curves of various pure PEG during the heating process](image)

![DSC curves of various pure PEG with during the freezing process](image)
### Table 2.3 Measured thermal properties of pure PEG with different molecular weights

<table>
<thead>
<tr>
<th>PEG</th>
<th>$T_m$ (° C)</th>
<th>$\Delta H_m$ (kJ/kg)</th>
<th>$T_f$ (° C)</th>
<th>$\Delta H_f$ (kJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEG(10000)</td>
<td>61.1</td>
<td>187.3</td>
<td>49.5</td>
<td>142.1</td>
</tr>
<tr>
<td>PEG(4000)</td>
<td>57.7</td>
<td>186.7</td>
<td>36.3</td>
<td>152.2</td>
</tr>
<tr>
<td>PEG(1000)</td>
<td>32.9</td>
<td>173.4</td>
<td>30.1</td>
<td>154.3</td>
</tr>
<tr>
<td>PEG(800)</td>
<td>28.5</td>
<td>137.3</td>
<td>14.2</td>
<td>129.8</td>
</tr>
</tbody>
</table>

Figures 2.3 and 2.4 and Table 2.3 indicate that the latent heat of pure PEG with different molecular weights (800, 1000, 4000, 10000) ranged from 137.3 kJ/kg to 187.3 kJ/kg. The latent heat of PEG increased with the increase of molecular weights, proving that PEG has a large latent heat. From Table 2.3, it can be seen that the melting and freezing temperatures varied from 28.5° C to 61.1° C in the heating process, and from 14.2° C to 49.5° C in the freezing process for different molecular weights of PEG. The large range of melting temperatures makes it possible to use PEG in different applications.

### 2.3 Thermal properties of form-stable TES composites

#### 2.3.1 Preparation of TES composites

Form-stable composites of PEG/SiO$_2$ were prepared with different component ratios to investigate the maximum weight percentage of PEG in the composite. Figures 2.5 (a)-(c) show the photos of the main experimental devices used in the composite material preparation. Figure 2.5 (d) shows the samples that were made in the experiments.
2.3.2 Thermal property investigation

- Thermal enthalpy analysis

From Figures 2.6 and 2.7 and Table 2.4, it can be seen that the enthalpy of the composites decreased with the diminution of the weight percentage of PEG. Moreover, compared to the measured latent heat of the composite PCMs with the calculated value, it was found that the measured values were slightly lower than the calculated ones. This was because SiO$_2$ kept quite stable in the phase transition of PEG. Therefore, SiO$_2$ can be considered as an impurity in PEG affecting the perfection of the crystallization process. In addition, the melting and crystallizing temperatures had exhibited no significant change. Table 2.4 shows that compared to pure PEG, the change in melting temperature of the composite materials ranged from 0.43- 4.58° C, and the changes in freezing temperature were 1.16- 3.46° C. These changes were not significant for the practical application.
2. Design, modification and analysis of thermal energy storage materials

Figure 2.6 DSC curves of PEG/SiO\textsubscript{2} with different mass ratios during the heating process

Figure 2.7 DSC curves of PEG/SiO\textsubscript{2} with different mass ratios during the freezing process

Table 2.4 Measured thermal properties of the composite materials

<table>
<thead>
<tr>
<th>Composite Materials</th>
<th>Thermal properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_m$ (°C)</td>
</tr>
<tr>
<td>PEG(85wt. %)/SiO\textsubscript{2}</td>
<td>61.61</td>
</tr>
<tr>
<td>PEG(70wt. %)/SiO\textsubscript{2}</td>
<td>60.85</td>
</tr>
<tr>
<td>PEG(60wt. %)/SiO\textsubscript{2}</td>
<td>60.32</td>
</tr>
<tr>
<td>PEG(50wt. %)/SiO\textsubscript{2}</td>
<td>56.60</td>
</tr>
</tbody>
</table>

- Phase change behavior analysis

From Figure 2.8(a), it can be seen that pure PEG was crystalline and its crystal structure was orbicular at 25° C. This indicates that polyethylene glycol had a good crystalline capacity, which contributed to the reasonable latent heat. When the temperature reached 64°C in the heating process, the color became faint and parts of the crystal structure disappeared. This was because parts of PEG started to melt and the crystal structure was consequently damaged. No color light appears in Figure 2.8(c). This indicates that the entire quantity of PEG was almost melted completely at 68° C. In other words, the phase change process was finished at this point. The whole process occurred quickly, indicating that PEG has a narrow melting temperature range from 60° C to 68° C. The results were in good agreement with the results of the DSC analysis. In the freezing process, when the temperature dropped down to 54° C, the crystalline light reappeared. Compared to the photo at the same temperature during the heating process (Figure 2.8 (b)), the color turned lighter. The same observations can be found in the photo image when temperature dropped to 25°C. The results show that PEG has a subcooling problem and its crystal structure cannot be recovered completely.
Figure 2.8 POM photos of pure PEG during the heating and freezing processes (X200): (a) 25° C (heating process), (b) 60° C (heating process), (c) 64° C (heating process), (d) 68° C (cooling process), (e) 54° C (cooling process) and (f) 25° C (cooling process).

Figure 2.9(a) shows the POM photo image of the composite material at 25° C. Unlike the pure PEG, the orbicular shape of the crystal structure cannot be observed in the composite materials due to the limitation of the supporting materials. However, the colored lights representing the PEG crystalline can still be seen in the photo. With the temperature rising, the color becomes faint. The POM micrograph of the composite PCMs at 120° C is shown in Figure 2.9(d). At this point, all the light has disappeared and solid particles can still be found in this last stage. This indicates that SiO₂, serving as a supporting material, helped prevent leakage of the melted polyethylene glycol. This solid–solid phase-change behavior of the composite is further confirmed by visual observation. When the composite was slowly heated to 120° C, it was observed that liquid leakage did not occur during the process. In the freezing process, the color reappeared but was lighter than it was at 25° C.
2. Design, modification and analysis of thermal energy storage materials

- Thermal stability analysis

Figure 2.9 POM photos of pure PEG during the heating and freezing processes (X100): (a) 25°C (heating process), (b) 60°C (heating process), (c) 64°C (heating process), (d) 120°C (heating process), (e) 54°C (cooling process) and (f) 25°C (cooling process)

<table>
<thead>
<tr>
<th>a)</th>
<th>b)</th>
<th>c)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="a" alt="Image" /> 25°C (heating process)</td>
<td><img src="b" alt="Image" /> 60°C (heating process)</td>
<td><img src="c" alt="Image" /> 64°C (heating process)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>d)</th>
<th>e)</th>
<th>f)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="d" alt="Image" /> 120°C (heating process)</td>
<td><img src="e" alt="Image" /> 54°C (cooling process)</td>
<td><img src="f" alt="Image" /> 25°C (cooling process)</td>
</tr>
</tbody>
</table>

Figure 2.10 illustrates TG results of the SiO₂, PEG, and PEG/SiO₂ composites, respectively. From the figure, it can be seen that the supporting material, SiO₂, was quite stable during the measuring temperature range from 0°C to 800°C. No mass losses occurred in it during the heating process. In contrast, pure PEG lost its weight starting at 227°C. When the temperature reached 358°C, there was almost nothing left of PEG, which means that it combusted and decomposed completely before that point. Hence, PEG can be used safely below a temperature of 227°C. For the composite materials, the curves show that the weight loss occurred at 300°C as the PEG in the composite started to vanish. Up to 310°C, the mass fraction did not change. PEG mass fractions in the two composites can be obtained at 82.7 wt. % and 84.5 wt. %, respectively.
Thermal cycle tests

In this experiment, the composite material at PEG mass proportion of 85 wt.% was chosen for testing its stability of thermal performance after 1, 150, and 300 periods of thermal cycling. Figure 2.11 and Table 2.5 show the detailed results of the PEG/SiO$_2$ composites and thermal properties after repeated thermal cycles. It can be seen that for all cycles, the melting temperatures of composite PCM changed by 0.17° C and 3.18° C, and the freezing temperature changed by 1.62° C and 2.97° C, respectively. It can be seen that the form-stable composite PCM has good thermal reliability in terms of the latent heat. The latent heat of melting changed by 4.1% and 2.7%, while the latent heat of freezing changed by 7.3% and 4.9%, respectively, which indicated that PEG and its composites had a quite good thermal stability.

Figure 2.11 DSC curves of the TES composites under thermal cycles
2. Design, modification and analysis of thermal energy storage materials

Table 2.5 Measured thermal properties of the composite materials under thermal cycles

<table>
<thead>
<tr>
<th>Cycles</th>
<th>$T_m$ [°C]</th>
<th>$\Delta H_m$ [kJ/kg]</th>
<th>$T_f$ [°C]</th>
<th>$\Delta H_f$ [kJ/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>61.61</td>
<td>162.9</td>
<td>48.36</td>
<td>124.2</td>
</tr>
<tr>
<td>150</td>
<td>60.78</td>
<td>156.2</td>
<td>46.74</td>
<td>116.9</td>
</tr>
<tr>
<td>300</td>
<td>58.43</td>
<td>158.5</td>
<td>45.39</td>
<td>118.1</td>
</tr>
</tbody>
</table>

2.4 Enhanced thermal conductivity by AlN modification

2.4.1 Preparation

Due to the hydrolysis of AlN, two coupling agents were selected to modify the surface AlN particles. Different coupling agents were dissolved in different solvents. Ethanol and isopropanol served as solvents for the silane coupling agent (KH550) and NDZ-401 coupling agent, respectively. First, the two coupling agents were dissolved in 100ml of solvent. Then, the solution was added to a three-neck flask connected with a water-condensing unit. Subsequently, 20g of AlN was added to flask and stirred. The flask was heated in a water bath at a given temperature (50, 60 and 70°C) for three hours. After washing and filtering, the powder was dried at 110°C. Finally, 1g of treated powder was taken and put into 50ml water at 60°C. The performance of modification of AlN was conducted by pH measurement. After that, the modified AlN was added during the composite preparation with different ratios, and thermal conductivity was tested using a Hot Disk device.

2.4.2 Mechanism of modification on AlN

- Hydrolysis of AlN Powder

The hydrolysis of AlN can produce aluminum hydroxide and ammonia. The reaction of AlN powder with water at room temperature is illustrated by the following scheme[83-85]:

$$\text{AlN} + 3\text{H}_2\text{O} = \text{AlOOH} \text{ (amor)} + \text{NH}_3 \quad (1)$$

$$\text{NH}_3 + \text{H}_2\text{O} = \text{NH}_4^+ + \text{OH}^- \quad (2)$$

$$\text{AlOOH} + \text{H}_2\text{O} = \text{Al(OH)}_3 \quad (3)$$

AlN powder first reacts with water to form amorphous hydroxide (pseudoboehmite, AlOOH). Subsequently, amorphous aluminum hydroxide recrystallizes to bayerite (Al(OH)$_3$). Consequently, this hydrolysis process will damage the thermal conductivity performance of AlN. Therefore, it is necessary to modify the AlN surface to avoid hydrolysis.

- KH550 coupling agent

$\gamma$-aminopropyl triethoxy silane, NH$_2$(CH$_2$)Si(OC$_2$H$_5$)$_3$(KH550), was used as a coupling agent to modify the surface of AlN. The structural formula of KH550 is shown in Figure 2.12.
The silane coupling agent undergoes chemical changes during hydrolysis as shown Figure 2.13. When the KH550 meets with water, the SiOCH3 group transforms to the Si-OH group. Each Si-OH group in the coupling agent is supposed to react with one hydroxyl group of the β-AlN particle surface and form a covalent bond [86-89].

![Figure 2.13 Proposed schematic of modification mechanism for KH550: (a) Hydrolysis of KH550; (b) modification of AlN](image)

- **NDZ-401 coupling agent**

Another coupling agent used was C_{44}H_{96}O_{10}TiP_{2} (NDZ-401), and the structural formula of NDZ-401 can be seen in Figure 2.14.

![Figure 2.14 The structural formula of the NDZ-401 coupling agent](image)

The modification mechanism is illustrated in Figure 2.15. It can be seen that the NDZ-401 coupling agent has two different types of groups. One of these is (CH3)2CHO-, which reacts with the hydroxyl group of β-AlN particle surface and forms a covalent bond[89-91].
2.4.3 Performance of modification on AlN

- Comparison of AlN powder with and without modification

Figures 2.16(a) and (b) show the AlN powder mixed with water before and after modification. Because AlN reacts easily with water, Figure 2.16(a) shows the powder precipitated immediately when it was put into the beaker. In contrast, Figure 2.16(b) shows that the treated powder was quite stable on the surface of water, which was confirmed by pH measurements.

Because of the hydrolysis, a large amount of –OH groups were produced. By measuring the pH value of the suspension, it can be seen that the pH value quickly reached a maximum value of about 10. Consequently, KH550 and NDZ-401 were used to modify the surface of the AlN to prevent its hydrolysis. To test the anti-hydrolysis performance of the modified AlN powder, the pH values of the suspension were measured and compared. If the pH value was small, it indicated that the modified AlN had a good hydrolysis-resistance performance. Some parameters affecting the hydrolysis-resistance performance were also discussed.

![Figure 2.16 Photos of AlN aqueous suspension before and after modification](image)

(a) Before  (b) After

Figure 2.16 The photos of AlN aqueous suspension before and after modification

- Effect of the amount of coupling agent

Figures 2.17 (a) and (b) show the effects of two coupling agents on the pH values of the AlN aqueous suspensions. It can be seen in Figure 2.17 (a) that as the mass fraction of the KH550 increased from 1wt.% to 7 wt.%, the pH values decreased, which means the hydrolysis-resistance
performance of the AlN powder was enhanced. When the mass fraction was 5 wt.%, the pH value of the aqueous suspension was quite stable at around 8.5 for 26 hours. When the mass fraction was as high as 7 wt.%, the pH value of the aqueous suspension was measured at 7.6, without any change during the same time. In contrast, the pH value jumped from 6.5 to 9.5 in five and ten minutes when the mass fraction of KH550 was 1 and 3 wt.%, respectively. This means that the surface of AlN was not completely modified. Therefore, for KH550, the optimum mass fraction is 7 wt.% in this experiment. From Figure 2.17 (b), the same trend of mass fraction vs. pH value can also be observed for another coupling agent, NDZ-401. The difference is that for NDZ-401, only more than 2.5 wt.% of the mass fraction can reach a pH-stable aqueous suspension. For the experiment, 3 wt.% of NDZ-401 can be considered as the optimum mass fraction.

Figure 2.17 Effect of agent amount on AlN modification: (a) KH550; (b) NDZ-401

- Effect of reaction temperature

In this section, the reactions between the coupling agents and AlN were carried out at various temperatures. The results obtained are shown in Figures 2.18 (a) and (b), respectively. It was found that reaction temperature had a stronger impact on KH550 than on NDZ-401. With a rise in temperature from 50° C to 70° C, the pH value decreased with the enhanced anti-hydrolysis performance of modified AlN. Therefore, in this experiment, 70° C is recommended as the appropriate reaction temperature.
2. Design, modification and analysis of thermal energy storage materials

2.4.4 Thermal conductivity enhancement and analysis

Thermal conductivities of the composite PCMs were improved by using β-Aluminum nitride additive as a heat transfer promoter due to its high thermal conductivity. The conductivities increased with the increase of the AlN mass proportion. However, latent heat decreased after

---

Figure 2.18 Effect of reaction temperature on the AlN modification: (a) KH550; (b) NDZ-401

- Comparison of various coupling agents

Testing the optimum operation condition for each coupling agent, KH550 (7 wt. %, 70°C) and NDZ-401 (3 wt. %, 60°C), the results are compared and shown in Figure 2.19. Compared with an unmodified AlN aqueous suspension, both agents definitely contributed to the enhancement of anti-hydrolysis performance. According to the pH values of the stable suspensions, NDZ-401 produced a better modification on AlN.

Figure 2.19 Comparison of the PH values of modified AlN aqueous suspensions using various coupling agents
adding AlN powder in the composite. The optimal AlN weight percentage is 15% with the consideration of both thermal conductivity and heat capacity.

![Figure 2.20 Effect of added AlN amount on thermal conductivity](image.png)

### 2.5 Comparison of AlN-modified PEG/SiO$_2$ and PEG/EG

Two types of the TES composites were prepared using physical methods, and most of their thermal performance was similar. Hence, the results and analysis are not presented in this thesis. A comparison of the two composites is described in Table 2.6.

Two types of composite materials were prepared in two different ways. AlN-modified PEG/SiO$_2$ was prepared by blending two components in an aqueous solution and modified by adding AlN powder. PEG/EG was prepared by mixing melted PEG and EG together. In a comparison of the two methods, the preparation process of the PEG/EG took less time than the modified PEG/SiO$_2$. Both composites were easy and simple to prepare. The PEG/EG composite had quite a high thermal conductivity (1.324 W/m K) in comparison to the modified PEG/SiO$_2$, which would have a strong affect on heat transfer in practical applications.

<table>
<thead>
<tr>
<th>Descriptions</th>
<th>Modified PEG/SiO$_2$ (AlN=15wt. %)</th>
<th>PEG/EG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Materials</td>
<td>PEG and Silica gel (AIN additive)</td>
<td>PEG and expandable graphite</td>
</tr>
<tr>
<td>Reaction Category</td>
<td>Physical method</td>
<td>Physical method</td>
</tr>
<tr>
<td>Preparation methods</td>
<td>Blend PEG with silica gel and AlN in aqueous solution, and then dried.</td>
<td>Melted PEG mixed with EG</td>
</tr>
<tr>
<td>Preparation time</td>
<td>More than 27 hours</td>
<td>Around 3 hours</td>
</tr>
<tr>
<td>Maximum latent heat</td>
<td>Approx. 137.7 kJ/kg</td>
<td>Approx. 161.2 kJ/kg</td>
</tr>
<tr>
<td>Melting temperature</td>
<td>60.4 °C</td>
<td>61.46 °C</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>Approx. 0.5136 W/m K</td>
<td>Approx. 1.324 W/m k</td>
</tr>
</tbody>
</table>
2.6 Summary

In this chapter, the preparation of form-stable AlN-modified PEG/SiO$_2$ and PEG/EG composites was done using two physical methods separately. In the structure of these two composites, PEG served as the phase change material, and SiO$_2$ and EG served as a supporting material and matrix. AlN was added into PEG/SiO$_2$ for thermal conductivity enhancement.

Through DMA, POM and TG measurements, AlN-modified PEG/ SiO$_2$ and PEG/EG composites showed promising form-stable characteristics when the temperature was higher than the phase transition temperature of PEG.

For PEG/SiO$_2$ composites, the maximum weight percentage of PEG was optimized as 85 wt. % without any leakage, with a maximum latent heat of PEG/SiO$_2$ of 162.9 kJ/ kg.

KH550 and NDZ-401 were added to modify the surface of AlN. Compared with KH550, NDZ-401 modified AlN powder showed higher thermal conductivity enhancement. When adding 15wt. % of AlN into PEG/SiO$_2$ composite, the thermal conductivity improved by 73.37%, but the latent heat decreased to 137.7kJ/ kg.

Another PEG/EG composite was made by blending polyethylene glycol with expanded graphite. In this composite, the maximum weight percentage of dispersed PEG was optimized as 90 wt. % (enthalpy = 161.2 kJ/kg) without any leakage during the phase transition. Moreover, PEG/EG showed a reasonable thermal conductivity of 1.324 W/m· K.

To sum up, due to the large latent heat and high thermal conductivity, an EG-organic PCM-based composite has much potential for use in an indirect-contact TES container as a component of the M-TES system.
3. Thermal behavior demonstrated with Lab-scale M-TES system

When compared to that of an indirect-contact TES container, a direct heat transfer rate is larger due to the straightforward mixing between PCMs and HTO. A lab-scale M-TES system was designed, built and tested to investigate the dynamic thermal behavior of PCMs and the performance of the direct-contact TES container. This chapter is based on Paper VI.

3.1 Experiment

3.1.1 Materials

Erythritol and Thermia oil C were used as TES material and heat transfer media, respectively. The Erythritol was purchased from Bin Zhou San Yuan Biotechnology CO., LTD, Qing Dao, P.R. China. Erythritol (molecular formula: $\text{C}_4\text{H}_{10}\text{O}_4$) is a natural sugar alcohol (a type of sugar substitute) which has been approved for use in the United States and many other countries. Erythritol is a good choice for use as a thermal energy storage material and does no harm to the environment. The Thermia oil C was purchased from the Shell Company. Thermia Oil C is based on carefully selected and highly refined mineral oils that provide superior performance in heat transfer systems, and it has better capacity for heat transfer with a lower viscosity. In the static experiments, an oil-bath test was conducted at MdH for repeated heat storage and release tests (Figure 3.1). Erythritol was put into the glass tube heated in the oil bath. After the Erythritol melted completely, the glass tube was cooled down naturally. This experiment focused on the thermal stability of Erythritol and its sub-cooling phenomenon.

![Figure 3.1 Setup of oil-bath based thermal test](image-url)
3.1.2 Lab-scale M-TES system

Figure 3.2 illustrates the direct-contact M-TES system. In these dynamic tests, an electrical heater worked as a heat source during the charging process. Another water cycle was also built into the system to serve as the end user, where the cooling water was heated by the hot oil through a heat exchanger during the discharge process. Ten thermocouples were located in different positions of the TES container, and inlet and outlet of oil and water cycle. Two pressure meters were placed for monitoring the pressure change during the charging and discharging processes. At the beginning of the heat charging process, V1, V2, V5, V6 and V8 were closed. HTO was first heated by the electrical heater and stored in the two containers. When the oil temperature reached a set point, V1 and V2 opened and HTO was pumped into the TES container through the two bottom pipes. Then, HTO flowed out from the five holes of each bottom pipe to contact and melt Erythritol directly. Gradually, all the solid Erythritol melted completely. Due to the different densities of HTO and liquid Erythritol, they separated from each other. Lighter HTO was on the top phase, and flowed out from the top pipe of the TES container. In the discharging process, V3, V4, V7 and V9 were closed. Meanwhile, the water cycle started to operate. Through the heat exchanger, the cool water was heated by hot oil.

Figure 3.2 Sketch of the direct-contact M-TES system

Figure 3.3 shows photos of the experimental setup of lab-scale M-TES system built at MdH. The compact testing system was designed and installed on a small trailer with limited room. The TES container was designed as a cylinder tank with the dimensions of 200 mm in length and 800 mm in diameter (100 l of the container volume). The container was made of steel with a transparent glass cover mounted in the front. Erythritol was packed at the bottom of TES container and made up 50% of the TES container volume. Two bottom pipes were 60 mm above the bottom of the TES container with five holes downwards. The horizontal distance between the two pipes was 200 mm. One top pipe was 60 mm from the top of TES container with three holes upwards. There were two
3. Thermal behavior demonstrated with Lab-scale M-TES system

tanks for storage of hot oil, one tank to allow for the expansion during the heating process, and one tank to allow for storage of cooling water. In addition, one oil pump and two water pumps were installed to adjust the flow rate of oil and water with the use of one oil flow meter and one water flow meter. The whole system was covered by insulation cotton outside.

Figure 3.3 Photos of the experimental facility built at MdH

Energy input was calculated according to the oil temperature difference of inlet and outlet of the TES container. The theoretical maximum heat capacity of the TES container is obtained by three parts including the sensible heat capacity of Erythritol, the latent heat capacity of Erythritol and the sensible heat capacity of oil in the TES container. The detailed energy calculation can be done by the following equations [31, 44, 55, 70, 92-94]:

In the charging process:

\[ Q_{\text{oil,in}} - Q_{\text{oil,out}} = Q_{s,pcm} + Q_{l,pcm} + Q_{\text{oil,cont}} + Q_{\text{loss}} \] (1)

\[ Q_{\text{cont}} = Q_{s,pcm} + Q_{l,pcm} + Q_{\text{oil,cont}} \] (2)

\[ Q_{\text{cont}} = Q_{\text{oil,in}} - Q_{\text{oil,out}} - Q_{\text{loss}} \] (3)

\[ = \int_0^\tau [M_{\text{oil}} C_{p,oil}(T_{\text{oil,in}} - T_{\text{oil,out}})/3600] \text{d}t - \int_0^\tau \frac{S_{\text{cont}} K_{\text{ins}} (T_{\text{wall}} - T_{\text{room}})}{3600 + 1000 + Th_{\text{ins}}} \text{d}t \]

In the discharging process:

\[ Q_{\text{oil,out}} - Q_{\text{oil,in}} = Q_{\text{cont}} - Q_{\text{loss}} \] (4)

\[ Q_{\text{cont}} = Q_{\text{oil, out}} - Q_{\text{oil, in}} + Q_{\text{loss}} \] (5)

\[ = \int_0^\tau [M_{\text{oil}} C_{p,oil}(T_{\text{oil,out}} - T_{\text{oil,in}})/3600] \text{d}t - \int_0^\tau \frac{S_{\text{cont}} K_{\text{ins}} (T_{\text{wall}} - T_{\text{room}})}{3600 + 1000 + Th_{\text{ins}}} \text{d}t \]
3.2 Results and discussion

- Sub-cooling behavior of Erythritol

200 cycles of heat storage and release cycles were tested using Erythritol, and the melting points are illustrated in Figure 3.4. The results showed that Erythritol had sub-cooling problems, with its melting temperature ranging from 45 to 110°C. Hence, this issue will be focused on in the following dynamic tests on the TES container.

![Figure 3.4 Tests of repeated heat storage and release cycles](image)

- Performance of the TES container in the charging process

To investigate the effect of the flow rate of hot oil on the performance of the TES container in the charging process, three different flow rates of oil (21.0, 15.8 and 9.2 l/min) were selected and compared (Table 3.1). Results show that the flow rate affected the charging time for melting Erythritol. A higher flow rate increased the heat exchange rate, thus solid Erythritol melted faster. This is especially important for the final stage of the experiment. The higher flow rate contributed to melting Erythritol near the wall of the TES container, which affects the heat capacity of the entire container in the limited charging time during practical applications. It can be seen that the two phases were easily separated, indicated by phases in two different colours. This means the two phases were separated quite well due to their sizeable density difference. In addition, a higher flow rate resulted in a thicker foam layer, and the top pipe design should take this foam layer position into consideration.
3. Thermal behavior demonstrated with Lab-scale M-TES system

### Table 3.1 Comparison of the charging processes at different flow rates of oil

<table>
<thead>
<tr>
<th>Test</th>
<th>Parameters</th>
<th>60min</th>
<th>150min</th>
<th>210min</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>F_{oil}=21.0 l/min</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
</tr>
<tr>
<td>2</td>
<td>F_{oil}=15.8 l/min</td>
<td><img src="image4.png" alt="Image" /></td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
</tr>
<tr>
<td>3</td>
<td>F_{oil}=9.2 l/min</td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
<td><img src="image9.png" alt="Image" /></td>
</tr>
</tbody>
</table>

- **Performance of the TES container in the discharging process**

In the discharging process, tests were also conducted at different flow rates of oil (14.6, 10 and 5.3 l/min) at the same flow rate of cool water (10 l/min). Results are presented and compared in Table 3.2. During the discharging process, no sub-cooling phenomenon occurred, which proved that this issue could be overcome by dynamic heat exchange. From the pictures of different tests, it is clear that no crystal exists at the top part of the TES container. Results also indicated that the flow rate of oil affected the solidification time of Erythritol in the TES container. The higher the flow rate of oil applied, the shorter the discharging period was. Moreover, the oil flow was not blocked until the end of the heat release process.
Table 3.2 Comparison of the discharging processes at different flow rates of oil

<table>
<thead>
<tr>
<th>Test</th>
<th>Parameters</th>
<th>15 min</th>
<th>30 min</th>
<th>60min</th>
</tr>
</thead>
</table>
| 1    | $F_{\text{oil}}=14.6\text{L/min}$  
[f_{\text{water}}=10\text{L/min}] | ![Image](image1.png) | ![Image](image2.png) | ![Image](image3.png) |
| 2    | $F_{\text{oil}}=10\text{L/min}$   
[f_{\text{water}}=10\text{L/min}] | ![Image](image4.png) | ![Image](image5.png) | ![Image](image6.png) |
| 3    | $F_{\text{oil}}=5.3\text{L/min}$  
[f_{\text{water}}=10\text{L/min}] | ![Image](image7.png) | ![Image](image8.png) | ![Image](image9.png) |

3.3 Summary

In this section, a lab-scale of the M-TES system was set up in the laboratory to study the dynamic characteristics of Erythritol and the performance of the direct-contact TES container.

In the initial static experiments, Erythritol was found to have serious sub-cooling phenomena due to the difference (from 45 to 110 °C) between its melting and freezing points. However, in the lab-scale M-TES system, the sub-cooling problem was solved by using the direct-contact container, due to dynamic heat exchange. Erythritol was mixed directly with heat transfer oil in the direct-contact TES container. Two liquid phases were separated quite well due to the big difference of material density. A net-like foam layer was observed in-between the two phases.

During the charging process, the bottom pipe was initially blocked and it took 90 min to make breakthrough. The melting time needed was affected by the flow rate of the HTO. The higher the flow rate, the shorter the charging time required. It took additional time to melt Erythritol, which stuck to the wall of the TES container. In the discharging process, crystals appeared in the foam layer initially. The solidification was also affected by the flow rate of the HTO. A shorter discharging time was required for a higher flow rate of HTO. No crystals were observed at the top phase of the TES container.

In the experiment, one half of the TES container was Erythritol, and another half was HTO. The theoretical heat capacity of the TES container in the experiment was 13.1 kWh (Erythritol was 74 kg and oil was 42 kg). By increasing the flow rate of the HTO, less input energy was required
during the charging process. Moreover, more heat was released with the increased heat flow rate of the HTO.

To sum up, due to a higher heat exchange rate between HTO and PCM, along with no sub-cooling problem, a direct-contact TES container can be used confidently in the M-TES system.
Mobilized thermal energy storage for heat recovery for distributed heating
4. Systematic study of scaling-up M-TES system for distributed heating

A mobilized thermal energy storage system is a potential solution for the recovery of industrial waste and excess heat to be used for distributed heating. In this chapter, a case study was investigated from both an economic and a technical perspective for the delivery of heat from a CHP plant to a small village. This chapter is based on Papers IV and V.

4.1 Feasibility study of M-TES system for distant heat delivery

4.1.1 Studied case and boundary conditions

- Information about the end user and the industrial heat source

In this case study, industrial heat was supplied to a sparse rural area. Ärla, a small village outside the town of Eskilstuna in Sweden, is 20 kilometres from a combined heat and power (CHP) plant in Eskilstuna. A small district heating network in the village is used for hot water supply during the summer, and for space heating and tap water during the winter. Currently, the village is heated by a 1 MW pellet boiler and two oil boilers of 4 MW each (only one of them is in use at any one time). DH in Ärla is connected to a number of buildings including a school, a childcare centre, a block of sheltered housing flats for older people, and several detached houses.

Figure 4.1 Location of heat supplier and end-user

The CHP plant, located in Eskilstuna, Sweden, is chosen as the heat supplier in the following feasibility study. The CHP plant has a major wood-fuelled KVV boiler to produce steam for electricity and heat production, and the other four oil boilers are responsible for producing heat for the peak load in the winter. In addition, another independent wood boiler operates in the winter and also during the maintenance period of the KVV boiler to supply heat to the DH network. Meanwhile,
the energy company also provides oil and pellets to local heat supply systems in small residential areas. Heat in the CHP plant is assumed to be derived from the combination of hot-water (85°C) in the accumulator and extracted steam (180°C) from the two wood boilers. Hot water from the accumulator can be thought as a cost-free heat source, and thus it can decrease the cost of charging heat for the M-TES system.

- Heat supply system description

A scheme of the existing and modified heat supply system is illustrated in Figure 4.2. In the existing system, an accumulator holds 200 m³ of hot water. The system is designed with a maximum heat load of 4.4 MW at 70–100 °C with 3.5 bars pressure. When the accumulator is fully charged, heat storage capacity reaches 14 MWh. The heat supply temperature is about 75 °C during the summer and 70–100 °C during the winter. The temperature of return water from local end users is about 35–40°C. The efficiencies of the pellet and oil boiler are 70% and 90%, respectively.

![Figure 4.2 Scheme of the existing and modified heat supply system in Årla](image)

In the modified heat supply system, a TES container from the M-TES system is added into the existing system. Cool water is first preheated through the TES container, and then heated up to the required temperature in the pellet boiler. Heat demand is mostly covered by M-TES system and the pellet boiler, and an oil boiler fuelled with bio oil is used only during the pellet boiler maintenance period.

4.1.2 Methods

Two systems are presented: the existing heat supply system, where heat is supplied by a pellet boiler and two oil boilers, and the modified heat supply system, where the heat supply comes primarily
4. Systematic study of scaling-up M-TES system for distributed heating

from the M-TES system and a pellet boiler, with an oil boiler as a backup. Annual transportation costs and heat supply by the M-TES system are calculated. An economic assessment of the modified heat supply system was conducted, including net present value (NPV) and payback period (PP) estimation. Sensitivity analysis was also made comparing NPV results on six parameters, including TES material cost, the cost of charging and discharging stations, heat supply cost for the M-TES system, pellet cost, heat selling price (in Ärla), and the electricity selling price.

4.1.3 Results and discussion

• Results of modified heat supply system

All the results have been calculated based on the use of Erythritol as a PCM and HTO as heat transfer medium in a direct-contact TES container.

In the M-TES system, the heat capacity of a TES container is 4.4 MWh. The energy efficiency of the M-TES container is assumed to be 85%, and thus one TES container finally can release 3.74 MWh of heat to end users with the consideration of 10.7 kWh of heat loss during each transportation. Two TES containers are charged and discharged every day, and 224 MWh of heat can be delivered each month. In the modified heat supply system, the annual heat supply of M-TES system is 2,444 MWh/y, which accounts for 42% of the total heat load of 5,883 MWh/y in Ärla. Meanwhile, pellet and bio-oil cover the local heat demand by 55% and 3%, respectively. In the CHP plant, it is assumed that additional 10% of the heat capacity of TES containers is needed during the charging process, and hence the charging heat totals 3,194 MWh. In Sweden, the total cost of renting a lorry is 73 €/h (offered by the transport company). Assuming a 1.5 hour trip between the CHP plant and the end user and 660 transportation cycles need annually, the annual transportation cost is 73,260 €/y.

Under the existing heat supply system, the annual fuel cost sums up 430,110 €/y including the costs of Pellets (159,700 €/y, 37%), oil (256,990 €/y, 60%) and bio-oil (13,420 €/y, 3%), respectively. By comparison, under the modified heat supply system, the annual fuel cost is 317,290 €/y including the cost of pellets (162,550 €/y, 51%), bio-oil (14,410€/y, 5%) and heat of M-TES system (140,330 €/y, 44%), respectively. Thus the heat cost under the existing system is 76 €/MWh, while that of the modified system is 56 €/MWh. This is a difference of 26%, which is significant.

• Different scenarios analysis

Two different scenarios were analyzed and compared to the existing heat supply system. In Scenario 1, the heat supply system consists of a pellet boiler, an M-TES system and a bio-oil boiler; in the M-TES system, TES containers are charged by cost-free heat from industrial plants. In Scenario 2, two oil boilers are replaced by a pellet boiler and all the heat is covered by two pellet boilers. By comparison, heat supply cost had a large reduction in Scenario 2, if M-TES system can deliver cost-free industrial heat to local end users. In Scenario 3, the heat supply cost also decreased by 20% when a new pellet boiler was installed. This indicates that an M-TES system will be more economically feasible and have a sizeable potential to supply heat when
Mobilized thermal energy storage for heat recovery for distributed heating

Cost-free industrial heat is available.

Table 4.1 Local heat supply with different scenarios

<table>
<thead>
<tr>
<th>Descriptions</th>
<th>Base case</th>
<th>Scenario 1</th>
<th>Scenario 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Produced heat amount</td>
<td>Pellet</td>
<td>Oil</td>
<td>Bio-oil</td>
</tr>
<tr>
<td></td>
<td>3194</td>
<td>2514</td>
<td>175</td>
</tr>
<tr>
<td>Unit cost (€/MWh)</td>
<td>35</td>
<td>92</td>
<td>69</td>
</tr>
<tr>
<td>Total fuel cost (€)</td>
<td>430110</td>
<td>250,220</td>
<td>294,200</td>
</tr>
<tr>
<td>Maintenance (€)</td>
<td>18,300</td>
<td>12,000</td>
<td>12,000</td>
</tr>
<tr>
<td>Sum (€)</td>
<td>448400</td>
<td>262,220</td>
<td>306,200</td>
</tr>
<tr>
<td>Heat supply cost (€/MWh)</td>
<td>76</td>
<td>43</td>
<td>52</td>
</tr>
</tbody>
</table>

* Pellet boiler efficiency is 70% and oil boiler efficiency is 90%*

4.2 Simulation on the integrated CHP plant with M-TES system

4.2.1 Charging process design in the CHP plant

The TES container of the M-TES system is charged in the CHP plant and then delivered. The option of integrating the CHP plant with the M-TES system is an important one. In the steam cycle of the CHP plant, live steam drives turbines to produce electricity, and various kinds of steam are extracted from different stages. The extracted steam can be used to heat the TES container. Meanwhile, the hot water in the accumulator of the CHP plant is also used as a heat source. Thus, four options (I to IV) in the CHP plant were proposed using hot water or extracted steam to heat the TES container (presented in Table 4.2).

Table 4.2 Description of the four options for heating the TES container

<table>
<thead>
<tr>
<th>Options</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Heated by hot water from an accumulator</td>
</tr>
<tr>
<td>II</td>
<td>Heated by live steam extracted from HPST</td>
</tr>
<tr>
<td>III</td>
<td>Heated by live steam extracted from LPST</td>
</tr>
<tr>
<td>IV</td>
<td>Heated by hot water heated by live steam from HPST</td>
</tr>
</tbody>
</table>

The scheme of the integrated CHP plant and the M-TES system is illustrated in Figure 4.3. There are two sites (Site 1 and Site 2) that were chosen to extract live steam. In Option II and Option IV, steam was extracted through a valve 1 (V1). In Option II, the TES container was charged through Exchanger 1. In Option IV, part of the hot water from the accumulator controlled by valve 3 (V3) was first heated by the extracted steam through Exchanger 1, and then the TES container was charged by Exchanger 2. In Option III, the steam was extracted through valve 2 (V2) to heat the...
TES container.

![Diagram of integrated CHP plant and M-TES system](image)

**Figure 4.3 Scheme of the integrated CHP plant and M-TES system**

### 4.2.2 Methods

To investigate the integrated M-TES system in an existing CHP plant, computational simulations were conducted to analyze different options for charging the M-TES system in the plant itself. First, information on the operating process was collected from the plant (in Eskilstuna), including data on operating conditions, heat and power productions and the heat supply load, to simulate and validate the modeling. Second, computational models of the CHP plant were developed using steady-state Aspen Plus software and validated with the data collected from the plant. Finally, the performance of the integrated CHP plant was evaluated with the different options based on power and heat output.

### 4.2.3 Results and discussion

Figures 4.4 (a) to (d) compare the impacts of the three options (Options II to IV) on the CHP plant with different amounts of heat supplied to the M-TES system, including power output, flow rate of steam extraction, heat supply and income of power, heat supply in the DH, and heat supply of the M-TES. By comparing these options for steam extraction, the power output followed the order Option III > Option IV > Option II, while the heat supply amount from the DH network followed the order Option II > Option IV > Option III. In addition, income served as an important indicator for the power plant. The impact on the plant’s income was thus analyzed as well; these incomes consisted of incomes of electricity, heat supply in the DH, and heat supply of the M-TES. Assuming that the price of electricity and the heat are 540 and 520 SEK/MWh, respectively, and then Option IV
generated the largest incomes among the three options (Figure 4.4(d)). Therefore, from an economic perspective, Option IV can be considered to be the best for the integrated system.

![Figure 4.4 Effect of steam-extracting options on the CHP plant including: (a) power output, (b) heat output, (c) steam-extracting flow rate and (d) income of electricity and heat production](image)

4.3 Summary

A feasibility study for using an M-TES heat supply system combined with a pellet boiler system to recover industrial heat from a CHP plant in order to meet the heating demands of a sparse area was conducted. Four options for heating the TES container were proposed and then compared by systematic simulation using Aspen Plus.

Results showed that two TES containers delivered a maximum heat of 224 MWh every month, which is to say, 2,444 MWh of heat annually. This amount can cover 42% of the total local heat demand. Economic analysis showed it is economically feasible to build the modified heat supply system, with a payback period of 6 years at the discount rate of 6%. A sensitivity study analyzed the effect of six parameters on a modified heat supply system. Results show that heat selling price had strongest impact on the economic feasibility of the modified heat supply system. However, cost-free heat sources are easy to be realized to make the M-TES system more feasible. In addition, in this case
TES containers can be charged with heat at different temperature based on four options, which affects the thermal performance according to the choice of TES materials. Based on the temperatures in the four options, the M-TES system was suitable to supply heat for sparse areas with Options II and IV, and to detached buildings with Options I and III. The power output decreased in the order Option III>Option IV>Option II, while heat supply to the DH network decreased in the order Option IV>Option II>Option III. Considering income from electricity, heat supply to the DH and heat supply to the M-TES system, Option IV can be considered the best one for the integrated system.
Mobilized thermal energy storage for heat recovery for distributed heating
5. Conclusions

In the first part of this thesis, three form-stable composites were prepared including PEG/SiO₂, AlN-modified PEG/SiO₂ and PEG/EG.

PEG/SiO₂ showed the advantage of preventing liquid PEG leakage during the solid-liquid transition with some reduction (trade-off) of latent heat when using the support of SiO₂. The maximum weight percentage of PEG in the composites is 85 wt. % with a latent heat of 162.9 kJ/kg. The latent heat was decreased by 13% compared with pure PEG. A linear relationship was found between latent heat and weight percentage of PEG.

To improve thermal conductivity, AlN was added to PEG/SiO₂ and linked by a coupling agent. Agent NDZ-401 showed a better anti-hydrolysis performance than agent KH550. However, adding AlN powder decreased the weight percentage of PEG in the composite and resulted in a decrease of latent heat in the composites.

Another form-stable PEG/EG composite was studied, which had maximum latent heat of 161.2 kJ/kg. By comparison, AlN-modified PEG/SiO₂ and PEG/EG composites were prepared using different physical preparation methods. The preparation of PEG/EG had fewer operating steps with less time needed. However, PEG had a certain sub-cooling, which led to the different melting and freezing temperatures. The PEG/EG composite showed much higher thermal conductivity than PEG alone (an increase of 343%). This indicated that the composite TES materials based on expanded graphite had potential for practical application. For the recovery of industrial waste or excess heat, EG-based composites can be considered as heat storage materials in the indirect-contact TES container.

In the second part of this thesis, an experimental M-TES model was built and tested to systematically study the characteristics of PCM and the performance of the TES container.

In the initial static experiments, erythritol was found to have a sub-cooling problem in the repeated heat charging and discharging cycles. This can be avoided by shaking the liquid phase when the temperature is close to freezing. In the dynamic charging process, the melting time needed was affected by the flow rate of the HTO, and the higher flow rate decreased that time needed. Two liquid phases were separated easily due to their difference in density. A net-like foam layer was formed between the two phases. In the discharging process, sub-cooling did not occur in a dynamic way. The solidification was affected by the flow rate of the HTO, and the higher flow rate decreased the discharging time needed. No crystalization was observed at the top of the TES container. A higher HTO flow rate decreased the input energy needed during the charging process. In the discharging process, higher heat can be released with the larger heat flow rate of HTO.

In the third part, the feasibility study of using an M-TES system within a modified heat supply system was analyzed, including technical analysis of the performance of the modified system, the
options for the heat charging process in the CHP plant, and the economic evaluation of the modified system.

It may be concluded that the M-TES system has the potential to deliver additional heat from an existing CHP plant, which can help cover the heating demand in rural areas. From both an economic and an environmental viewpoint, the M-TES system can also viably replace costly oil and reduce the amount of CO₂ emissions.

In the case study, two TES containers delivered maximum heat of 224 MWh every month, and the M-TES system supplied 2,444 MWh/y of heat, which covered 42% of the total local heat demand in a small village. In comparison, the heat cost of the modified system is 26% lower than that of the existing system.

In the CHP plant itself, the TES containers can be charged with heat from four sources: from hot water in the accumulator, from live steam extracted from HPST, from live steam extracted from LPST, and from hot water heated by live steam from HPST. The power output and heat output in the DH network decreased and the flow rate of steam extraction increased with the increase of charging heat from the CHP plant. By way of comparison, heat from hot water heated by live steam from HPST may be considered as the best option for use in the integrated system.
6. Future work

Mobilized thermal energy storage systems are a potentially effective way to deliver industrial waste heat to sparse areas or detached buildings, in combination with other forms of energy. PCM-based TES technology plays a key role in the performance of the whole system, and determines the feasibility of its practical application. The M-TES system also extends TES application possibilities and enlarges the commercial market for TES technology. The lab-scale M-TES system has been studied systematically in this work. However, there remain issues for future investigation. The following work is recommended for future study:

The structure of the direct-contact TES container should be modified, taking into consideration three aspects. (1) Resolve the initial block problem during the charging process. In our current system, it is difficult for hot transfer oil to get through the solid PCM materials above the bottom pipes, because there is no channel in the solid block to allow HTO to pass through. It is small ribs or pipes connecting the bottom pipes be placed evenly around the holes on the pipes. Thus when HTO flows out from the bottom pipe, it can go up along these ribs or pipes. (2) Decrease the melting time required during the charging process. In our system, the central part of the solid PCM was melted easily and quickly. However, much time was required to melt those PCM close to the container wall at the final stage. It is recommended to optimize the numbers and installing position of bottom pipes by modifying the structure. (3) Increase heat release during the discharging process. It is recommended that the discharging time be extended to increase heat release. Therefore, the dynamic uprising liquid reduces fast precipitation and the accumulation of crystals at the bottom of TES container.

It is recommended that an indirect-contact TES container be designed and compared to the performance of a direct-contact container. The main challenge for the indirect-contact container is lower charging and discharging power. The operating conditions of the TES container should be optimized based on heat storage and release data. The structure of the container can be optimized considering different types of immersed heat exchangers, including pipe numbers, pipe location, different types of pipe, etc., where heat transfer enhancement and heat capacity of the TES container should be well balanced.

It is important to further study proper phase change materials for across different charging temperature ranges. Inorganic PCMs were not studied in this thesis, but they are quite suitable for a TES container. It is critical for PCMs to be derived that involve less sub-cooling, and less phase separation, as well as less toxicity and corrosion.

It would be interesting to compare direct- and indirect-contact TES containers and determine which is more suitable for practical applications. Experiments on a lab-scale M-TES system combined with a pellets boiler system or an automatic control system are recommended. It is also recommended that a middle-size TES container be built and that a scale-up demonstration be implemented. For the M-TES system, the specific operating conditions should be optimized based
on the condition of the industry plant and the requirements of the end users.
7. Acknowledgements

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Mobilized thermal energy storage for heat recovery for distributed heating
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Mobilized thermal energy storage for heat recovery for distributed heating


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