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A review on supercooling of Phase Change Materials in thermal energy storage systems

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ABSTRACT

Thermal energy storage is at the height of its popularity to harvest, store, and save energy for short-term or long-term use in new energy generation systems. It is forecasted that the global thermal energy storage market for 2015–2019 will cross US$1,300 million in revenue, where the highest growth is expected to be in Europe, Middle East, and Africa followed by Asia-Pacific region. Thermal energy storage has become an inevitable component of fluctuant renewable energy systems due to their significant role in increasing efficiency and Quality of Service (QoS).

Currently, one major research stream in such systems is improving the efficiency of heat exchangers and heat carriers. Hence, studying thermal behavior and thermophysical properties of heat storages is of great importance. In this study, we review a common but not very well-known problem of supercooling of Phase Change Materials (PCM). Supercooling is a thermophysical property of PCMs that is problematic in thermal storage applications. This review looks at supercooling from another point of view and investigates applications (such as specialized thermal storage applications) that can put supercooling into operation. To achieve this, development of techniques to increase state stability and designing reliable and stable supercooled heat storage systems will be investigated. The study will look at the thermal energy storage of supercooled liquids, degree and measurement of supercooling. Furthermore, factors that influence degree of supercooling and their effect on output capacity will be discussed. It looks at the supercooled material in four major categories and looks into the mechanisms for triggering crystallization in supercooled liquids. Applications including solar thermal storage will be the discussed in details. From the results discussed in this review researchers will identify and gain insight into supercooling control techniques, which are necessary for developing efficient heat exchangers, and also essential for promoting adoption of sustainable renewable energies.

1. Introduction

Thermal energy storage systems are becoming particularly important for enhancing system reliability and Quality of Service (QoS) in new energy generation systems. Storing heat from renewable energy sources in thermal energy devices and providing it in the case of energy shortage or voltage sags enhances the overall system efficiency and promotes share of renewables in the energy mix. Use of solar energy as an energy source for PCM devices was started dates back to 1942 [1]. Current pervasive and entrenched use of thermal storage is well reflected in the report of the Global Thermal Energy Storage Market 2015–2019, which forecasts it will cross US$1,300 million in revenues by 2019 where Europe, the Middle East and Africa are expected to witness the highest growth followed by Asia-Pacific region [2].

The thermal energy storage systems store thermal energy for consumption at a later time for heating or cooling applications or even power generation. They use sensible heat, latent heat or heat from thermo-chemical processes. Examples of sensible heat storage are liquid and air based systems, which use water and rock bed for heat storage, respectively [3,4]. Another example is using refractory bricks for heat storage in load levelling applications [5]. These heavy bulky bricks are also known as night storage heaters because they heat space during the day from the stored heat during the night. The sensible heat storages have low energy density and variable discharging temperatures. Hence, they are not efficient when compared with storage devices that involve latent or thermo-chemical heat storage process [6].

Abbreviations: PCM, Phase change material; QoS, Quality of Service; PV, Photovoltaic; SAT, Sodium acetate trihydrate; PEG, Polyethylene glycol; PCMMC, PCM microcapsules; MF, Melamine Formaldehyde; DSC, Differential Scanning Calorimetry; HVAC, Heating, ventilation, and air conditioning; COP, Coefficient of Performance

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Table 1
Performance comparison of sensible, latent, and thermo-chemical thermal storages [9].

Thermal system	Capacity (kW h/t)	Power (MW)	Efficiency (%)	Storage period (h, d, m)	Cost (€/kW h)
Sensible heat	10–50	0.001–10	50–90	d/m	0.1–10
Latent heat	50–150	0.001–1	75–90	h/m	10–50
Thermo-chemical heat	120–250	0.01–1	75–100	h/d	8–100

Thermal energy is also found in supercooled liquids where the material is in thermal equilibrium with its surroundings. The stored latent heat of fusion is released by triggering the crystallization of the supercooled liquid. Currently, latent heat storage which can be absorbed or released during the melting and solidifying process of Phase Change Materials (PCMs) is known as the most efficient way to store cold energy [7] or for heat recovery [8]. To show the advantages of the latent heat over the sensible heat, Hauer [9] conducted a comparison between the sensible heat storage of water, the latent heat storage and the heat from thermo-chemicals. Table 1 shows a comparison of capacity, power, efficiency, storage period and costs between latent, sensible, and thermos-chemical based systems. Based on the table, latent heat provides higher energy storage density compared to sensible heat based systems and less cost compared to techno-chemical based devices.

Having said all advantages of latent heat storage, poor stability of supercooled material have caused key problems in their applications. For instance, poor stability leads to degradation in thermal properties in long term cycling. Corrosion between supercooled liquid and its container [10], change in density [11], experiencing phase segregation are other leading problems.

Supercooling is “the delay in the start of solidification” and takes place whenever a PCM undergoes a phase change from liquid to solid [10]. It is a state where liquid PCM does not solidify immediately upon cooling below the freezing temperature, but start crystallization only after a temperature well below the melting temperature is reached. Thus, it is necessary to reduce the temperature below the phase change temperature to start crystallization and to release the latent heat. The latent heat is the largest proportion of charged thermal energy and would only release below the supercooled temperature [10]. During supercooling, sensible heat would be lost but latent heat is released instantly on crystallization. Supercooling and crystallization rate are categorised as kinetic properties of PCM [12].

Supercooling leads to reduced crystallization temperatures; thus the latent heat will be released at a lower temperature (wider temperature range) [13]. As a result, large temperature difference between charging and discharging is needed to fully utilize the latent heat, which is undesirable for efficient energy storage applications. Thus, supercooling is a key figure and a critical issue from the practical point of view and understanding the factors and methods to control supercooling is fundamental to advance thermal energy research and technology.

Presently, research on materials and product development of latent heat storages is carrying out by several developers. Broad review articles on latent heat transfer [14], and quite sizeable amount of works are reported on PCM applications [5]. Among these problems, there is no critically analyzed review article that deal with supercooling and related techniques to control partial melting process, adding nucleating agents or discussing unpredictable character of crystallization.

We will look into the thermophysical property data, simulations and experimental studies to identify short-term and long-term behavior of supercooled material through their useful life and thermal cycles. The heat transfer rate, effect of the supercooling level on heat recovery, effect of the rate of cooling on the degree of supercooling, and energy saving benefits with supressed supercooling material will be presented subsequently. In addition, we will present how supressing supercooling will help developers to incorporate PCMs into heating/cooling systems, and how the improvements will affect the final cost analysis in real life examples. Publications have used undercooling [10], subcooling [5] and supercooling [15] alternatively. We review all these works and consider these phrases (i.e. undercooling, subcooling and supercooling) as the same. It is expected that this article will fill the research gap in reviewing supercooling of PCM along with providing new future directions and potential applications on the topic.

2. Thermal energy storage of supercooled liquids

Supercooling is a *metastable state* of PCMs in which they remain in liquid phase when cooled below their melting point temperature. For instance, pure water can be cooled down to −41 °C at atmospheric pressure in the laboratory without taking place of transition into solid phase [16]. Fig. 1 shows a supercooled liquid and its solid state.

A supercooled liquid requires additional energy to release the stored latent heat. Hence, using supercooled liquid is not an efficient method in short-term applications. Nonetheless, supercooling is an interesting characteristic in long-term applications because supercooled liquid can be kept in a thermal equilibrium with the ambient temperature for a long period of time. During the initial cooling process, releasing the heat is inevitable but the remaining phase transition energy can be stored for extended periods of time without further loss of heat [15].

Supercooling is one of the very common phenomena in nature and technology processes but still new to researchers and developers. Water is the best known PCM when studying supercooling occurrences in nature. Small insects and fishes survive from freezing during the cold season by controlling crystallization in their system and taking benefit of supercooling. Examples of using supercooled water in technology are in thermal energy storage in solar systems or commercial heat pads for cold climates [8]. Details of research on supercooling in water is well-discussed in the literature [18].

Metastable supercooled liquids are extremely vulnerable to impurities and external disturbances. They are favourably disposed towards stable condition through forming a new phase. Thus, capability of a reliable nucleation when releasing the latent heat is very important [19]. In addition, supercooled material should have a large amount of activation energy for nucleation to avoid a spontaneous crystallization

Fig. 1. A supercooled liquid and its solid state [17].