Development of a Heat Storage Material for Elevated Temperatures

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Abstract

This paper describes the development and the properties of a new heat storage material for thermal storage around 120°C. The material is intended to be applied in a packed bed in direct contact to a heat transfer medium, e.g. air, water or glycol. Erythritol, Polyethylene and Adipic Acid turned out to be most suitable for an encapsulation with a polymeric coating. For the primary shaping casting and pressing were tried experimentally. The selection of the coating material took place under consideration of many aspects, in particular of a practicable coating technology. Silicone rubber was chosen as the preferred encapsulation material for a coating process which bases on injection moulding of half shells. A significant number of 32 mm diameter spheres for testing purposes were produced in a small series in laboratory scale. Various tests showed that the silicone encapsulated HDPE is the most promising material.

The new material is intended for example for the storage of solar heat for industrial process applications.

1. Introduction

In many cases of temporal mismatch of heat generation and heat demand thermal storage is the preferred measure to increase the energy efficiency of a technical system (e.g. [1]). Although more than 70% of the industrial heat demand arise at temperatures above 100°C, most thermal storage applications focus on temperatures below that level [2] and the application of Phase Change Materials (PCM) is not very common. It was the aim of our development to provide a heat storage material which

- works in the temperature range between 100°C and 160°C,
- increases storage density by avoiding the air pockets which are applied in encapsulated PCMs to restrict internal pressure variations during phase change,
- avoids the application of metal encapsulations.

The PCM balls were designed to be used as bulk material in a packed bed with different heat transfer media.

2. Choice of Materials

About 100 potential heat storage materials ($\Delta H \geq 150$ J/g) in the temperature range from 100°C to 180°C were found out and assessed according to practical aspects for heat storage like price, toxicological properties and supercooling. The results of this investigation are given in [3]. Another compilation can be found in [4]. Erythritol (melting point: 118°C), Polyethylene (HDPE, mp.: 126°C) and Adipic acid (mp.: 151°C) were chosen for the material development as a result of various tests. These tests included enthalpy measurements (Fig. 1, Erythritol does not solidify in the DSC vessel, Adipic acid shows extreme heat generation during solidification), cycling tests (Fig. 2, cut-out of the test of a 4 g HDPE sample), corrosion tests and investigations concerning chemical compatibility.

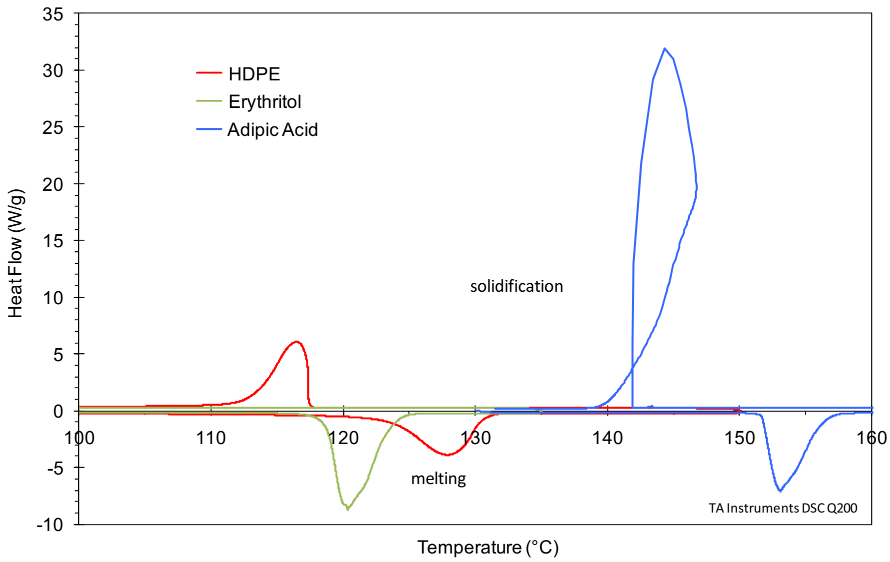

Fig. 1: DSC measurements of the preferred PCM materials

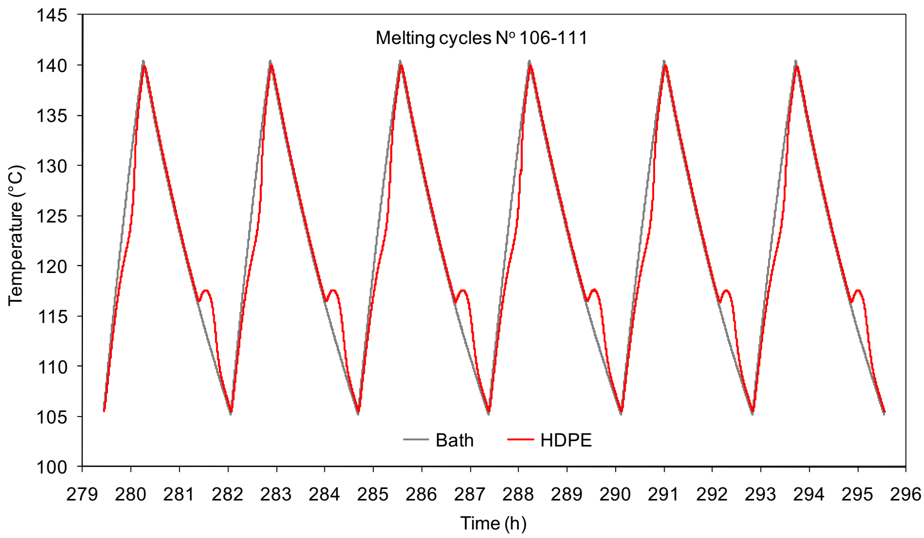

Fig. 2: Cut-out of the cycling test of a 4 g HDPE sample

3. Primary Shaping of PCM-Balls

It was decided to restrict the size of the PCM capsules to 32 mm in diameter in order to achieve sufficient heat transfer properties. Because coating of solid particles has a higher potential for economic up-scaling then filling of prefabricated hollow balls shape forming of the PCM was required. Two different techniques were applied to produce PCM-blanks with 30 mm diameter: casting and pressing. Pressing turned out to be advantageous for the high melting Adipic acid (steel die, application of a parting compound) whereas casting showed the best productivity for materials with lower melting points. The properties of the PCM-blanks are summarised in Table 1 (Relative density is given in relation to the solid matter.).

Table 1: Average Properties of the PCM-Blanks

Material	Technology	Diameter [mm]	Mass [g]	rel. Density [%]
Erythritol	Casting	30.31 ± 0.12	20.63 ± 0.37	97.3 ± 0.7
HDPE	Casting	29.65 ± 0.12	13.44 ± 0.16	99.5 ± 0.6
Adipic acid	Pressing	30.18 ± 0.05	19.30 ± 0.02	98.2 ± 0.5

4. Encapsulation Technology

The coating material has to fulfil a number of specifications which result from the application conditions:

- continuous utilization temperature (CUT) between 110°C and 160°C,
- mechanically stable and tight at CUT,
- chemically stable in water or water steam, oil or glycol at CUT,
- thickness of the coating: about 1 mm,
- stretching of the coating material during melting of the PCM: at least 6% but with remarkable safety margin,
- The temperature of the PCM during the coating process should not remarkably exceed its melting temperature (around 120°C or around 150°C, resp.).

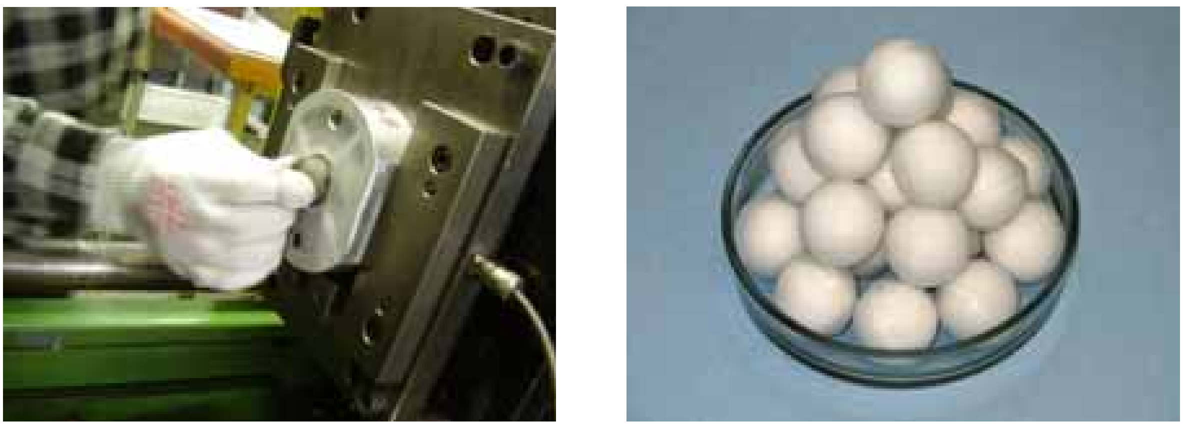

Fig. 3: Encapsulation of the PCM-Blanks (left) and PCM-Balls ready for Application

The last requirement turned out to be one of the most restrictive for the selection of the coating technology. After intensive testing of chemical and mechanical properties silicone rubber was chosen as coating material and an encapsulation technology was developed together with the company KET Kunststoff- und Elasttechnik GmbH (patent pending). PCM-Blanks were manufactured in laboratory and coating was carried out under industrial conditions in a single mould.

5. Characterization of the Storage Material

The coated PCM spheres were tested and measured concerning a variety of properties: geometric parameters, static mechanical pressure in molten state, dynamic mechanical stress in molten state, leak tightness, permeability, heat storage capacity, thermal cycling stability etc.

5.1. Geometric Parameters

The following Table 2 summarizes the average geometric parameters of the coated PCM balls.

Table 2: Average Properties of the single PCM balls

Material	Coating thickness [mm]	Total mass [g]	Mass fraction of PCM [%]
Erythritol	0.995	24.73	83.4
HDPE	1.18	18.01	74.6
Adipic acid	1.12	23.45	82.3

5.2. Mechanical Tests

The PCM balls are intended to be applied in a packed bed. There they undergo various mechanical impacts. Two different tests were carried out in the molten state to evaluate the mechanical load capacity of the balls: squeezing in a universal testing machine and churning under a rotating disc.

Fig.4: Non-deformed and deformed PCM-ball (left) and Set Up for churning test (1- furnace, 2 – motor and load, 3 – rotating disk, 4 – beaker, 5 – heat transfer fluid, 6 – support pad, 7 – PCM-ball

With the universal testing machine it was found that the balls can be pressed with 2300 N before a rupture of the coating occurred. The diameter was reduced by 81% in the direction of the force in the moment of rupture. Fig. 4 shows a ball with solidified PCM at 50% diameter reduction. In a packed bed with air as heat transfer fluid Erythritol balls deform by up to 25% in a 6 m height column. Heat transfer fluids with higher density allow correspondingly higher beds. For the churning test the balls were deformed in liquid PCM state by 33% by a disc which was rotating with 13 rpm (see Fig. 4). After 288 h of rotation at 134°C no damages could be found.

5.3. Thermal Properties

A calorimeter was set up to measure the thermal properties of the PCM balls. It mainly consists of a glass Dewar vessel with a basket for the PCM balls, a heating element with power supply, a data logger with precise power meter and thermometer and a stirrer. Glycol was used as a heat transfer fluid. Fig. 5 shows as an example the temperature trend of the heat transfer fluid with 6 HDPE balls for a constant heating power (reduced after 1 hour) and without heating.

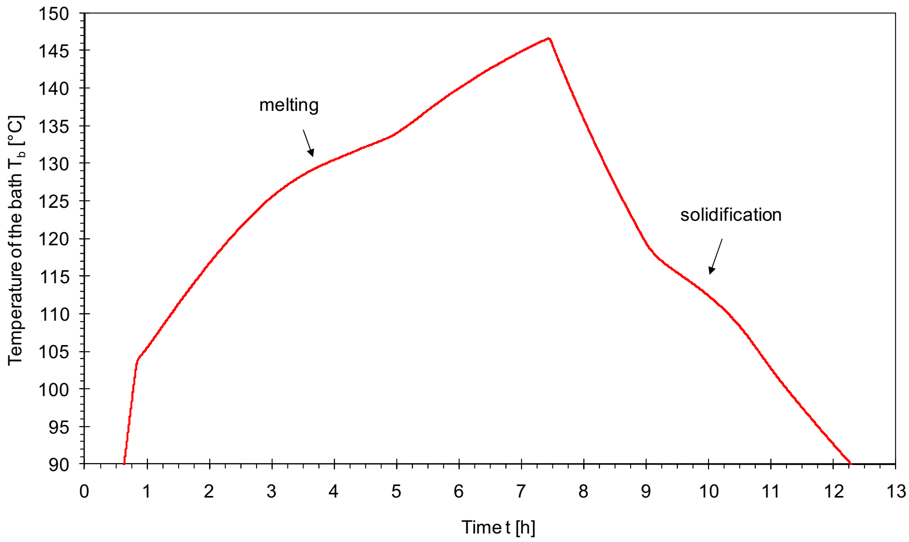

Fig. 5: Typical temperature trend for a calorimetric measurement (6 HDPE balls)

Melting and solidification enthalpies ΔH_m and ΔH_s as well as the heat transfer power values P_m and P_s could be determined after corrections for the thermal losses and the calorimeter constant. Fig. 6 shows exemplarily a drawing with the corrected introduced heat vs. the temperature of the bath. The measured thermal properties of the different (encapsulated) PCM balls are summarized in Table 3. Melting and solidification temperatures are mid-temperatures T_{mid} as indicated in Fig. 6. Heat transfer power values were calculated by differentiating corrected introduced heat Q with respect to time t. The given values are peak values for a heating rate of about 6 K/h and a cooling rate of about 10 K/h (The same rates influence the given temperature ranges.). Error spans (if given) result from statistics of multiple measurements. The volume related enthalpy in packed bed was calculated from the mean values of the mass related enthalpies of melting and solidification.

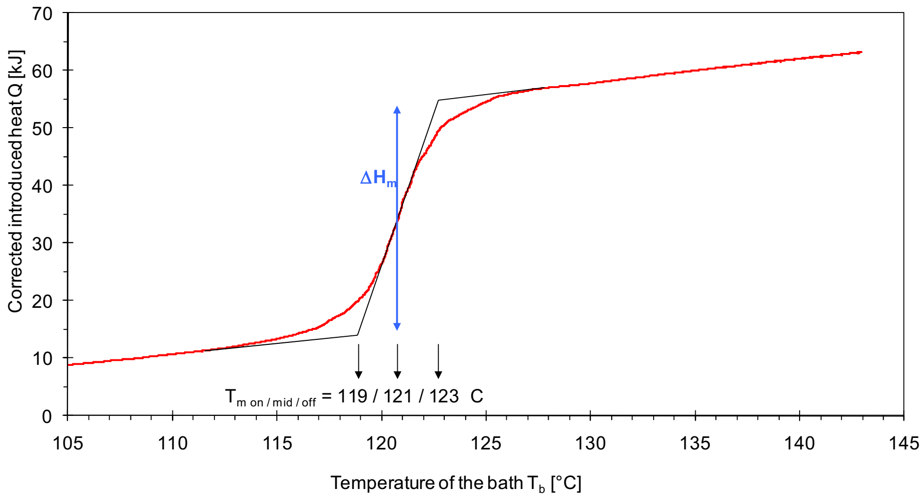

Fig.6: Determination of thermal parameters from caloric measurements

Table 3: Thermal properties of the Heat Storage Materials

	HDPE	Erythritol	Adipic acid
Melting Temperature T_{mmid} [°C]	130.5 ± 1	123 ± 2	155.5 ± 0.6
Melting Range T_{moff} - T_{mon} [K]	5	4	3.7
Solidification Temperature T_{smid} [°C]	116 ± 1	62 ± 12	143.8 ± 0.6
Solidification Range T_{son} – T_{soff} [K]	6		6.9
Melting Enthalpy ΔH_m [kJ/kg]	157 ± 23	281 ± 31	203 ± 21
Solidification Enthalpy ΔH_s [kJ/kg]	-165 ± 20		-200 ± 7
Volume related Enthalpy in packed bed (60%) ΔH_{ms} [kJ/l]	99 ± 14	231 ± 25	157 ± 11
Heat transfer power mel. P_m [W/kg]	22	24	38
Heat transfer power sol. P_s [W/kg]	-34		-55

5.4. Durability of the Heat Storage Material

A number of tests were carried out to evaluate the durability of the fabricated heat storage materials. It is well known that the permeability of silicone is relatively high in comparison to other polymeric materials. Therefore aging tests with glycol and air as heat transfer fluids were carried out. Encapsulated PCM balls were stored for more than 1600 h in the fluid at 132°C. Fig. 7 shows the results of periodic weighing.

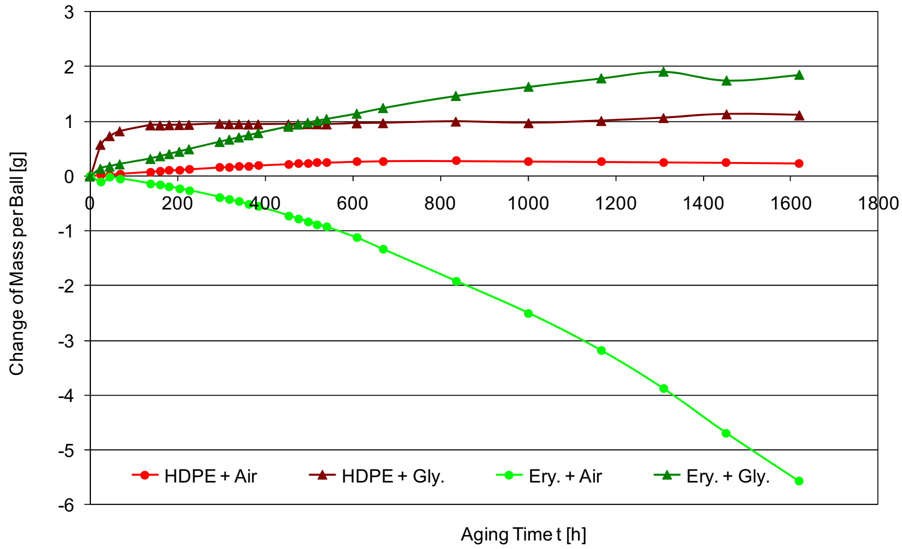

Fig. 7: Change of mass of PCM balls during aging test at 132°C in different heat transfer fluids

It can be seen that the Erythritol balls in air lose significant amounts of PCM. This material combination is therefore not suitable for long term applications. The same is true for Erythritol balls in Glycol. The fluid penetrates the balls and dissolves the Erythritol. For HDPE can be stated that the Glycol penetrates into the balls up to a certain amount. The increase of mass of HDPE balls in air is explained by oxidation effects.

Calorimetric measurements were carried out to evaluate the impact of aging on the different materials. The results of these measurements are shown in Fig. 8.

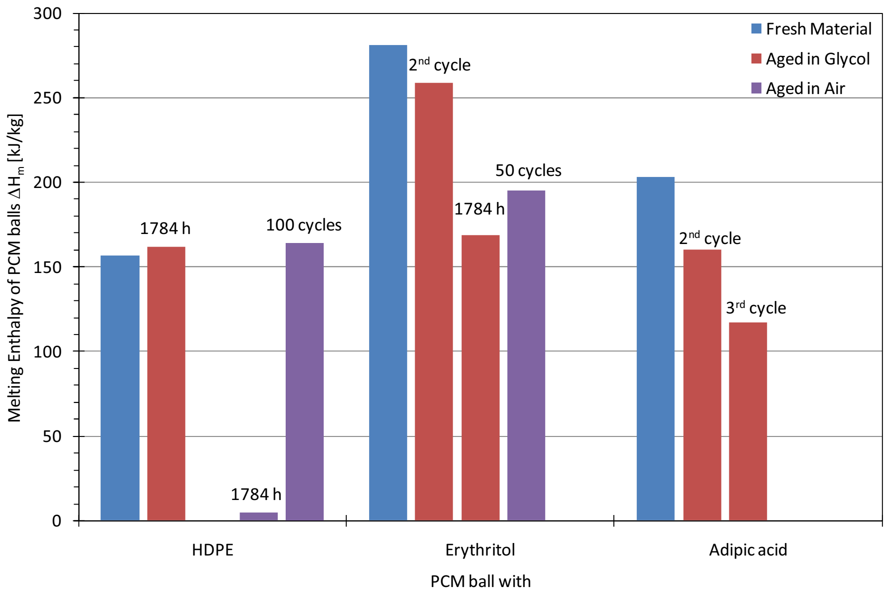

Fig. 8: Remaining melting enthalpy after different aging processes

Aging of HDPE in glycol has no effect on the storage capacity of the material. Short time influence of air (100 cycles took about 100 h) does also not affect storage capacity whereas long term influence of hot air degenerates the HDPE totally. Aging of HDPE balls in water (not shown here) gave promising results. The calorimetric investigations are not yet finished. Aging of Erythritol in Glycol reduces storage capacity considerably. This was already expected from the weighing results. Even short time air cycling leads to a noticeable reduction of the storage capacity. Aging of Adipic acid balls at 160°C in different media (including water) leads to a damage of the silicon coating after short time.

5. Conclusion

Different high temperature heat storage materials were encapsulated in silicone. Adipic acid in molten state turned out to be too aggressive to the silicone coating. Erythritol is a promising heat storage material due to its high volumetric storage density. Unfortunately silicone is too permeable to seal the sugar alcohol securely. Various experiments with nucleating agents to decrease supercooling brought only limited success. Silicone encapsulated HDPE balls are a promising material for thermal energy storage at elevated temperatures. The material is available with melting temperatures from about 80°C to 130°C. The long term contact of HDPE balls in molten state to air should be avoided.

ILK Dresden is looking for partnership and for a heat storage application at elevated temperatures, to demonstrate the capability of the newly developed material within a pilot project.

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