Durability of a fin-tube latent heat storage using high density polyethylene as PCM

Christoph Zauner¹, Florian Hengstberger¹, Mark Etzel¹, Daniel Lager¹, Rene Hofmann¹ and Heimo Walter²

¹ AIT Austrian Institute of Technology GmbH, Center for Energy, Sustainable Thermal Energy Systems, Giefinggasse 2, 1210 Wien, Austria
² Vienna University of Technology, Institute for Energy Systems and Thermodynamics, Getreidemarkt 9/BA, 1060 Wien, Austria

E-mail: christoph.zauner@ait.ac.at

Abstract. Polymers have rarely been used as storage materials in latent heat storages up to now. Thus, we systematically screened all polymers available on a large-scale, selected promising ones based on their theoretical properties and experimentally tested more than 50 candidates. We found that polyethylene, polyoxymethylene and polyamides are promising even as recycled material. Especially high density polyethylene (HDPE) turned out to be suitable as was shown by detailed thermophysical characterization including more than 1000 heating and cooling cycles for INEOS Rigidex HD6070EA. We built a storage with 170 kg HDPE and a total mass of 600 kg based on a fin-tube heat exchanger and characterized its energy capacity, power characteristics and temperature profiles using a thermal oil test rig. In total we performed 30 melting and crystallization cycles where the whole storage was above 100 °C for more than 140 hours. After usage we examined the interior of the storage by cutting it into various pieces. A thin layer of degradation was observed on the surfaces of the PCM which is most likely related to thermooxidative degeneration of HDPE. However, the bulk of the PCM is still intact as well as the heat exchanger itself.

1. Introduction
Thermal energy storages are necessary to increase the share of intermittent renewable energies and to enhance waste-heat recovery in industries with non-continuous processes and therefore they help mitigating CO₂ emissions [1], [2] by allowing for demand side management and load shifting [3], [4]. Because of their high energy density and the much lower pressure than steam accumulators or pressurized water tanks, latent heat storage above 100 °C are of particular interest. Many concepts and some demonstrators have been tested for concentrated solar power applications [5], [6], [7], [8], [9] [10]. Also there has been growing interest in the utilization of latent heat storages in industrial processes either for waste heat recovery or in combination with solar thermal collectors [11], [12], [13], [14], [15]. Even in solar cooling there have been investigations and demonstrators for storages not only on the cold, but also on the hot side of the cooling machine [16], [17]. For various applications, different phase change materials (PCMs) have been investigated and characterized [18], [19], [20], [21]. In most publications polymers have only been considered as shape stabilizing or encapsulation material [22], [23], but not as PCM itself. Only a few authors investigated polyethylene as storage material [24], [25], [26],...
[27], [28], [29], [30]. Thermal stability of HDPE has only been investigated for small samples via differential scanning calorimetry (DSC). Here, we present our findings for a lab-scale storage that has been above 100°C for more than 140 hours and was charged and discharged about 30 times.

2. Experimental Investigation

2.1. High density polyethylene as phase change materials

Polymers have various advantages as phase change material:

- there is a worldwide large-scale industry developing, producing and optimizing polymers
- there exist many different types and grades of polymers with melting points from below 80°C up to 300°C
- polymers can be compounded with many additives to improve their physical and chemical properties
- a vital recycling industry collects and processes polymers, which offers an interesting opportunity in terms of PCM costs

As described in more detail in [31], we systematically screened all polymers available on a large-scale, selected promising ones based on their theoretical properties and experimentally tested more than 50 candidates (polymers and polymer compounds). We found that the most promising types are polyethylene (PE), polyoxymethylene (POM) and various polyamide types (PA).

We do not know of any polymeric product that is mainly used in a temperature range above the melting point of the polymer. Thus, although the polymer industry is very experienced when it comes to ensure suitable long-term durability of their products, there is almost no information available on the thermal stability in an PCM storage-like environment.

Only few authors performed appropriate investigations: Waschull [27] investigated the aging of HDPE: 100 cycles in a DSC in air atmosphere between 105°C and 140°C (100 hours in total) and 1784 hours directly exposed to hot air or glycol (132°C) were performed. The material remained stable in glycol and over 100 DSC cycles, but degraded completely after 1784 hours direct exposure to hot air. Oezcan [29] investigated the aging of HDPE in an oven for up to 30 cycles showing only minor degradation and in direct contact with steam at 140°C, which however destroyed the material.

For our PCM storages, as is discussed in detail in [32], we chose HDPE because of its superior thermophysical properties for our investigations. Among the different polyethylene grades screened INEOS Rigidex HD6070EA showed the highest enthalpy.

To investigate the long-term durability of our material, we performed cyclic tests in a DSC (Netzsch DSC 204 F1). We sealed the PCM in a steel crucible under nitrogen atmosphere and exposed our polymer to more than 1000 heating and cooling cycles between 80°C and 160°C with a heating and cooling rate of 10 K/min. The result is shown in Figure 1 and indicates that the material may actually stabilize around 90% of the initial enthalpy.

Although DSC measurements are a relatively easy means to investigate thermal stability of a PCM, there are some drawbacks due to small sample size and heating/cooling rates possibly much different than in a real storage. Therefore, we continued our investigations with a lab-scale storage.

2.2. Lab-scale storage

The details of our storage, its experimental characterization and simulation is described in great detail in [32]. Here, we just briefly repeat some key facts: The storage consists of an insulated steel container which houses a fin-tube heat exchanger and HDPE as phase change material. The heat exchanger consists of 301 parallel fins made of the aluminum alloy AlMg2.5. The
Figure 1. DSC cycle test of HDPE INEOS Rigidex HD6070EA.

thickness of the fins is 0.25 mm and the fin spacing is 8 mm. The fins are attached to 72 tubes made of steel (1.0345), which are arranged in a staggered geometry shown in Figure 2. Two manifolds at opposing fronts of the storage provide the storage connections to the piping system and connect the tubes such that they are all flown through in parallel. As insulation we used 30 cm of mineral wool. The storage has a total length of 3.4 m and a weight of 370 kg without PCM.

Figure 2. Dimensions of a single aluminum fin showing the staggered arrangement of the steel tubes. At positions 1 to 5 thermocouples were immersed within the PCM.

In total, the storage was filled with 170 kg of HDPE pellets (Figure 3), which were melt using the immersed heat exchanger. Figure 4 shows the top surface of the PCM before the characterization campaign started.

We used a thermostat (Lauda ITH350) and the heat transfer fluid (HTF) Marlotherm SH to charge and discharge the storage. Inlet and outlet temperatures were recorded using Pt100 resistance thermometers (accuracy class 1/10 DIN) and the mass flow was measured using a clamp-on ultrasonic flow meter (Flexim Fluxus F601, measurement accuracy 1 %).
Figure 3. In total 170 kg of HDPE pellets were poured into the storage. Immersed thermocouples were used to measure the PCM temperature during storage operation.

Figure 4. Top surface of the full storage before the quantitative characterization was started.

Of course, storage power and capacity depend on the operating conditions (initial and final storage temperature, HTF inlet temperature and mass flow). As an example the power profile and storage temperatures are shown for charging and discharging between 105°C and 155°C (Figure 5).

The results of our lengthy characterization campaign are summarized in Table 1.

2.3. Analysis of the storage after characterization

During the whole characterization campaign we completed roughly 30 melting and crystallization cycles at ambient atmosphere conditions. In total, the whole storage was more than 60 hours above the melting range (around 130°C), more than 80 hours between 100°C and 130°C and more than 30 hours between ambient temperature and 100°C.

In order to analyze the state of the storage after the characterization campaign, we cut the storage into various pieces by water jet cutting (Figure 6).

It can be seen that the top surface of the HDPE became yellowish (please note, that the color on the pictures depends on illumination and camera set-up), which is most likely due to oxidation reactions. However this degradation layer is only very thin and the bulk of the PCM
Figure 5. Temperatures and calculated power profiles for a thermal oil mass flow of 0.41 kg/s.

![Temperatures and calculated power profiles](image)

| $T_{dc}$ ($^\circ$C) | $T_c$ ($^\circ$C) | $Q_{2\text{hours}}$ (kWh) | $q_{\text{vol}}$ (kWh/m$^3$) | $Q_{l,PCM}$ (kWh) | $Q_{s,PCM}$ (kWh) | $Q_{s,st}$ (kWh) | $Q_{s,alu}$ (kWh) | $Q_{s,ins}$ (kWh) | $\Delta H$ (kJ/kg) |
|----------------------|-------------------|--------------------------|---------------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| 85                   | 175               | 27.0                     | 92.7                      | 12.7             | 10.6             | 2.9              | 0.4              | 0.5              | 268.4            |
| 95                   | 165               | 23.6                     | 81.1                      | 12.4             | 8.2              | 2.3              | 0.3              | 0.5              | 261.6            |
| 105                  | 155               | 19.3                     | 66.3                      | 11.1             | 5.9              | 1.6              | 0.2              | 0.5              | 235.8            |

Table 1. Measured storage characteristics for a constant mass flow of 1.0 kg/s. The sensible energy stored was estimated according to $Q = mc_p(T_c - T_{dc})$ (c...charged, dc...discharged) for steel (st), aluminum (alu) and PCM (s...sensible, l...latent). The insulation (ins) was heated by an average of 15$^\circ$C. The latent part is the difference between the total energy, $Q_{2\text{hours}}$, and all sensible contributions. In the last column we estimated the resulting PCM-enthalpy.

Figure 6. Water jet cutting of the storage at LKR Ranshofen (Austria).

still looks intact (Figure 7).

Also, one can observe a pretty large cavity close to the center of the storage reaching down
to the bottom of the storage (Figure 8). The cavity spreads out over roughly 30 cm in the longitudinal direction of the storage. Another set of smaller bubble-like cavities occurs close to the storage outer walls. We can only speculate about the origins of these cavities: either they are related to the large volume contraction of the HDPE or there have been the degree of filling was insufficient from the very beginning onwards.

Figure 7. At the top of the storage there is a thin degradation layer, while the bulk of the PCM is still intact.

Figure 8. A large cavity close to the center and a few smaller one close to the storage wall can be observed.

The PCM forms a solid block with the heat exchanger (HEX) and can be easily removed from the storage (Figure 9). A degradation layer can also be observed on the surface of the PCM-HEX-block which was close to the storage wall. Again, the layer is rather thin and the bulk PCM is intact. Most likely, oxygen could flow downwards between the PCM-HEX-block and the storage wall and in combination with heat lead to thermo-oxidative degeneration of the HDPE.

Figure 9. A thin layer of thermo-oxidatively degraded HDPE is also observed for the PCM close to the storage wall.

Figure 10 shows a longitudinal cut through the center of the storage. The PCM bulk is still intact with the thin degradation layer at the top surface. Many small cavities especially in the upper half of the storage can be observed which again can be related to thermal expansion of the HDPE in its liquid state or to insufficient initial filling. The heat exchanger consisting of aluminum fins mounted onto steel tubes also look intact. The tubes show no distortion. The
fin spacing is also regular and is still the same as in the design of the heat exchanger. Only the lowest fins show significant distortion which is most likely related to mechanical stress induced during melting and crystallization due to thermal expansion of the PCM and/or the whole heat exchanger itself.

From Figure 11 one can infer that the fins are still in ideal thermal contact with the steel tubes. No detachment occurs which proves the suitability of the manufacturing method. We also removed some tubes from the PCM block. No degradation was visible below the tube or close to the fins within the bulk of the PCM.

![Figure 10. Longitudinal cut through the storage showing small cavities. The heat exchanger and the PCM bulk is still intact after the characterization campaign.](image1)

![Figure 11. Only the lowest part of the heat exchanger fins show some distortion.](image2)

3. Conclusion and Outlook

PCM storages can be used in many different applications with very different requirements in terms of storage capacity, charging and discharging power profiles, available charging inlet temperatures and demanded discharging outlet temperatures. Polymers are a widely available, cheap and versatile class of materials that have been rarely considered as PCM until now. After a thorough screening we identified PE, POM and various PAs as promising candidates and selected HDPE for more detailed investigations. We showed that it has a high phase change enthalpy and is thermally stable over more than 1000 cycles in a DSC. We designed a suitable heat exchanger, built a lab-scale prototype storage and characterized its energy capacity and power profiles for different operating conditions. After roughly 30 melting and crystallization cycles where the whole storage was above 100 °C for more than 140 hours, we examined the interior of the storage by cutting it into various pieces. A thin layer of degradation was observed on the surfaces of the PCM which is most likely related to thermo-oxidative degeneration of HDPE. However, the bulk of the PCM is still intact as well as the heat exchanger itself. In our ongoing work, we are currently investigating different applications (aluminum die casting, polymer extrusion, district heating networks) to identify the exact requirements for a storage. Based on a detailed monitoring we will adapt and optimize our current PCMs and storage design and plan to demonstrate how one can improve energy efficiency and reduce CO₂ emission utilizing new polymer-PCM storages.

Author Contributions and Acknowledgments

The Austrian Research Promotion Agency (FFG) is gratefully acknowledged for funding this work under Grant No. 838669 (StoreITup!) and under Grant No. 848914 (StoreITup-IF). C.
Z. conceived, submitted and leads the projects, performed the PCM screening, designed and characterized the storage with the help of M. E and F. H. GEA Klimatechnik built the storage. D. L. and C. Z. characterized the PCMs. M. E. performed his master thesis at AIT supervised by C. Z., F. H. and H. W. who is gratefully acknowledged for valuable discussions regarding storage design, simulation and characterization. R. H. is the PhD supervisor of C. Z. and is gratefully acknowledged for valuable discussions regarding characterization results. The paper was written by C. Z. and commented by all authors. Katharina Resch from the University of Leoben is gratefully acknowledged for ideas in the project development phase and material screening. Josef Reiter from LKR Ranshofen is gratefully acknowledged for cutting the storage.

References

[1] Cabeza L F, Miró L, Oró E, de Garcia A, Martin V, Kronauer A, Rathgeber C, Farid M M, Paksoy H O, Martínez M and Fernández A I 2015 Applied Energy 155 365–377

[2] Arce P, Medrano M, Gil A, Oró E and Cabeza L F 2015 Applied Energy 88 2764–2774

[3] Arteconi A, Hewitt N J and Polonara F 2012 Applied Energy 93 371–389

[4] Barzin R, Chen J J J, Young B R and Farid M M 2015 Energy 92 505–514

[5] Liu M, Tan N H S, Belusko M and Bruno F 2015 Energy Procedia 69 913–924

[6] Nathyanandam K and Pitchumani R 2014 Applied Energy 126 266–280

[7] Laing D, Bahl C, Bauer T, Lehnmann D and Steinmann W D 2011 Solar Energy 85(4) 627–633

[8] Bayón R, Rojas E, Valenzuela L, Zarza E and León J 2010 Applied Thermal Engineering 30(17-18) 2643–2651

[9] Pointner H and Steinmann W D 2014 Applied Energy 150 335–340

[10] Abe Y, Takahashi Y, Sakamoto R, Kanari K, Kamimoto M and Ozawa T 1984 J. Sol. Energy Eng. 465–474

[11] Syed M T, Kumar S, Moallemi M K and Naraghi M N 1997 Ashrae Journal 45–50

[12] Zauner C StoreITup! Final project report (2014) AIT Austrian Institute of Technology Vienna, Report may be retrieved on request from the corresponding author

[13] Zauner C, Hengstberger F, Etzel M, Lager D, Hofmann R and Walter H 2016 Applied Energy 179 237–246