Acta Polytechnica CTU Proceedings **38**:478–482, 2022
https://doi.org/10.14311/APP.2022.38.0478

Published by the Czech Technical University in Prague

DURABILITY OF LATENT HEAT STORAGE SYSTEMS

Sylva Bantová, Milan Ostrý*, Karel Struhala

Brno University of Technology, Faculty of Civil Engineering, Institute of Building Structures, Veveří 95, 602 00 Brno, Czech Republic

* corresponding author: ostry.m@fce.vutbr.cz

Abstract. Latent heat storage represents technology with significantly higher energy storage density. The thermal energy storage capacity of building structures and storage units integrated into building services contribute to the energy flexibility of buildings. This paper presents results from laboratory experiments focused on the compatibility of heat storage media represented by phase change materials (PCMs) with materials of container. Material compatibility of selected PCMs with the plastics and metals were tested by a long-term experiment. Two organic-based and two inorganic-based phase change materials were selected for tests of compatibility with selected metals (aluminium, copper and brass) and plastics (PP-H, PE-HD, and PVC-U). Plastic-PCM compatibility was determined by gravimetric method. For evaluation of metal-PCM compatibility, calculation of corrosion rate was applied. The less mass changes and lower penetration of PCMs to the matrix was observed for inorganic-based PCMs compared to organic-based PCMs. In case of compatibility between metals and PCMs, the highest values of corrosion rate were calculated for copper immersed in inorganic-based PCMs Rubitherm SP25.

Keywords: Phase change materials (PCMs), compatibility of materials, metal corrosion, mass changes, container, latent heat storage systems, durability, energy flexibility.

1. Introduction

The situation on the European energy market in 2021 which is accompanied by rising of energy cost is one of the reasons for the demand of larger energy independence and energy supply safety of energy consumers. When fossil fuels such as natural gas or coal are considered to be replaced by renewable energy sources (RES), the sufficient energy storage capacity should be employed. The reason is that energy production from RES, such as sun, is not constant in time. If the energy in the form of heat should be stored for short or longer time, then the sensible heat storage or latent heat storage technology should be integrated in energy grid. The amount of stored heat in sensible heat storage technology depends on the weight of storage medium, its thermal capacity and change between initial and final temperature. On the other hand, the latent heat storage represents advanced and much more sophisticated approach to heat storage. Materials suitable for latent heat storage are called phase change materials (PCMs). Latent heat storage technology uses the phase change of storage material and solid-liquid transformation is suitable for building applications. Due to the phase change, proper encapsulation of PCMs must be designed for all heat storage units with reasonable durability.

Durability and sustainability of each heat storage unit depends on the compatibility between the material of encapsulation and PCMs to avoid undesirable leakages of PCMs and their interaction with surrounding environment. This paper presents the results of compatibility tests of PCMs selected from organic or inorganic group, and plastics and metals that are suitable materials for their encapsulation.

2. Materials and Methods

2.1. Materials

A total of four PCMs were selected for testing: salt-hydrate-based Rubitherm SP22 and Rubitherm SP25 (representatives of the inorganic group) and paraffin-based Linpar 17 and Linpar 1820 (representatives of the organic group). Table 1 shows the selected PCM parameters. As all tested PCMs have a mean value of Peak temperature around 24 °C, the actual material range values of materials is 22–28 °C, this suggests the suitability of specific PCMs for integration into systems inside residential buildings due to similar indoor room temperatures.

Three common metals and plastics were selected for the experiment as potential encapsulation materials for PCMs. The reason for the selection was good market availability, the high value of thermal conductivity of metals and the wide use of plastics in the buildings for distribution systems of rainwater or sewer pipes, for storage tanks, etc. Two groups of samples were determined for the experiment:

- plastic group representatives: PP-H (polypropylene), PVC-U (polyvinylchloride) and PE-HD (high-density polyethylene);
- metal group representatives: Aluminium, Copper and Brass. Table 2 shows the parameters of tested metals.

	Type	Latent Heat [J g^{-1}]	Onset Temperature [°C]	Peak Temperature [°C]
Linpar 17	organic	152	21	22
Linpar 1820	organic	141	24	27
Rubitherm SP25	inorganic	122	18	28
Rubitherm SP22	inorganic	145	14	25

TABLE 1. The parameters of selected PCMs.

	Composition	Density [g cm^{-3}]	Thermal conductivity [W m^{-1}K^{-1}]	Area [cm^{-2}]
Aluminium (EN AW1050 H111)	Al99.5	2.70	230	
Copper (EN CW024A)	Cu-DHP-99.9	8.96	340	41.80
Brass (EN CW617N)	CuZn40Pb2	8.73	114	

TABLE 2. The selected parameters of the metal samples.

2.2. METHODS

The assessment of compatibility between selected PCMs and the metal/plastic samples is based on the weight changes of the samples with the calculation of the evaluation parameters separately for each material. The test procedure is based on the methodology of The American Society for Testing and Materials test G1-03 [1] and consists of the following parts:

- preparation of the samples – visual inspection, cleaning (with toluene for metals), dried, clearly labelled;
- weighing of samples – the samples were weighed with the analytical balance;
- immersion in PCMs – the samples were placed into the testing beakers and were poured with liquid PCMs, the test beakers were placed into incubator;
- thermal cycling in the incubator – the samples were exposed to repeating temperature cycling ranging from 15 °C to 40 °C, the cycle was divided into 4 parts, each lasting for two hours;
- removal from PCMs: the samples of one set were withdrawn from the testing beakers at the given time: after 7-28-84 days (for the metals) and every seventh day (for the plastic) of exposure to the PCMs, one set containing three pieces of samples;
- visual check (the changes of appearance) of samples;
- cleaning of the samples after removing;
- weighing of the samples;
- the selection of one sample from each set for subsequent calculations using the median value – to eliminate extreme values of the weight changes;
- the calculation of the parameters (the corrosion rate for metal, the percentage change in mass in case of plastic) and evaluation of the samples.

2.2.1. THE METHOD FOR EVALUATION OF THE METAL-PCM COMPATIBILITY

The corrosion rate (CR) was calculated for each metal sample in contact with the PCMs for a specified time, the procedure and the experimental conditions are given in Section 2.2. The CR methodology includes monitoring the mass loss of the metal samples relative to the surface area and the immersion time of the samples, CR is defined by Equation (1), described in [2, 3].

$$CR = \frac{\Delta m}{A \cdot (t_0 - t)}, \tag{1}$$

where CR is the corrosion rate in mg cm^{-2} year^{-1}, Δm is a mass loss in mg and it is defined by the equation $\Delta m = m(t_0) - m(t)$, where $m(t_0)$ is the initial weight of the sample before immersion to PCMs and $m(t)$ is the final weight after the immersion time, A is the surface area of the sample in cm^2 and $(t_0 - t)$ is the experimental immersion time of the samples in PCMs in years.

In this study, the calculated corrosion rates of the samples are compared to the classification described in The Guide for corrosion weight loss used in the industry [2, 4]. According to The Guide, PCMs are classified as compatible with the selected metal or incompatible, or compatible for a specific application. The suitability scales with the limit values and the verbal evaluation of CR are shown in Table 3.

The overall classification of the metal samples is supplemented by the calculation of the CR value defined according to the methodology described in [5, 6]. The calculation of the CR is based on The American Society for Testing and Materials test G-31 [7] as well, which determines the average CR values. The method is based on the weight changes that are caused by exposure of the samples to a corrosive environment during the experiment. This calculation procedure is not possible to use in case of localized corrosion on the surface of samples such as pitting or intergranular corrosion.

	Recommendation (verbal evaluation)
$CR = 50.0$ to $999.0\,\mathrm{mg\,cm^{-2}\,year^{-1}}$	Not recommended for service
$CR = 10.0$ to $49.9\,\mathrm{mg\,cm^{-2}\,year^{-1}}$	Caution recommended, based on the specific application
$CR = 0.3$ to $9.9\,\mathrm{mg\,cm^{-2}\,year^{-1}}$	Recommended for long term service

Table 3. The Guide for corrosion weight loss used in industry (the selected limit values) [2–4].

Material	**Immersion period**	**Linpar 17 (organic group of PCM)**			**Rubitherm SP25 (inorganic group of PCM)**		
		$\boldsymbol{\Delta m}$	$\boldsymbol{CR}$	$\boldsymbol{CR}$	$\boldsymbol{\Delta m}$	$\boldsymbol{CR}$	$\boldsymbol{CR}$
	[day]	**[mg]**	**[mg cm^{-2} year^{-1}]**	**[mm year^{-1}]**	**[mg]**	**[mg cm^{-2} year^{-1}]**	**[mm year^{-1}]**
Aluminium	7	0.800	1.049	0.00389	0.800	1.024	0.00379
	28	0.700	0.219	0.00081	0.900	0.292	0.00108
	84	0.500	0.053	0.00020	1.800	0.194	0.00072
Copper	7	1.400	1.807	0.00202	4.400	5.400	0.00603
	28	1.700	0.525	0.00059	5.800	1.863	0.00208
	84	1.600	0.174	0.00019	9.600	1.004	0.00112
Brass	7	1.300	1.685	0.00193	2.900	3.882	0.00445
	28	2.000	0.621	0.00071	3.200	1.061	0.00121
	84	0.400	0.044	0.00005	4.500	0.476	0.00055

Table 4. The corrosion rates values of tested metals exposed to effects of selected PCMs from the organic and inorganic group for periods 7, 28 and 84 days.

$$CR = \frac{K \cdot W}{A \cdot T \cdot D}, \tag{2}$$

where CR is the corrosion rate in $\mathrm{mm\,year^{-1}}$, K is a constant in $\mathrm{mm\,year^{-1}}$ that determines the resulting unit of the CR value (in our case $8.76 \cdot 10^4$), W is a mass loss in g, A is an area of a sample in $\mathrm{cm^2}$, T is a time of exposure in h and D is the density of materials in $\mathrm{g\,cm^{-3}}$.

2.2.2. The method for evaluation of the plastic-PCM compatibility

The criterion for evaluating plastic-PCM compatibility is the percentage change in mass of the tested samples. This parameter is determined by calculation according to the gravimetric method defined in the international standard [8] ISO 175:2000.

$$\Delta m = \frac{(m_t - m_{t_0})}{m_{t_0}} \cdot 100, \tag{3}$$

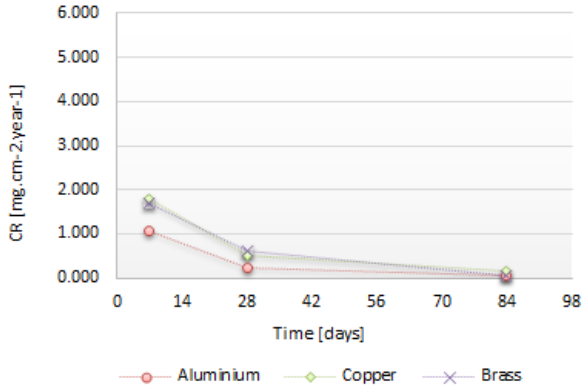
where Δm is the percentage change in mass in %, m_t is the weight of the sample after removal from PCMs in mg and m_{t_0} is the initial weight of the sample before immersion in PCMs in mg.

3. Results and Discussion

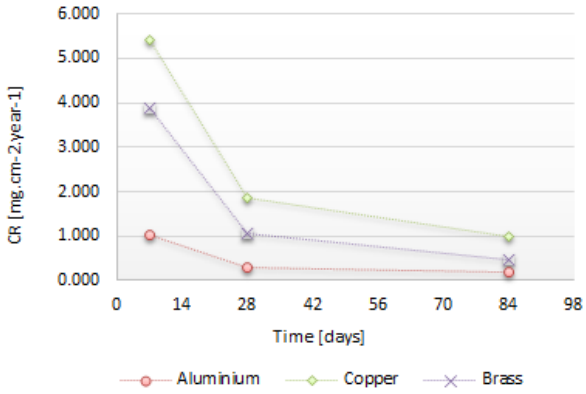
The material compatibility of the selected four PCMs with the plastics and metals was verified by a long-term experiment. The samples of both metals and plastics were immersed in the PCMs for the same period with a difference in their extraction frequency. Metals were extracted three times throughout the experiment, plastics every 7 days. This time cycle is similar by Moreno [3] and Óro [2]. In both cases, the evaluation procedure included the visual inspection of the surface changes and the weight changes of the individual samples before and after removal from the PCMs, followed by calculations of the evaluation criteria.

After removing the metal samples from the PCM, it was found that the samples immersed in inorganic PCM showed visual changes on their surface compared to the samples immersed in organic PCM. All metal samples were tarnished as early as one week after immersion, more pronounced changes were discovered on the surface of the copper samples.

The results of the test for metal-PCMs pairs are shown in Table 4. The table shows only the representatives of the two groups whose weight changes were higher compared to the other material in the group. The evaluation criterion is the corrosion rate that was calculated according to Equation (1) and (2). In general, the samples immersed in the organic PCM group showed smaller weight changes and lower CR values (see Table 4) than samples immersed in the inorganic group. These results are consistent with our initial assumption and also with the conclusions presented in the previous studies [3, 4]. The most significant mass loss occurred in the samples immersed in PCM Rubitherm SP25 (inorganic PCM), the highest values were achieved in the case of the copper, where the CR exceeded $5.4\,\mathrm{mg\,cm^{-2}\,year^{-1}}$ with the value mass loss of 4.4 mg. The CR curves of metal samples immersed in Rubitherm SP25 are shown in Figure 1b. The CR curves of all metal samples in inorganic PCMs (Figure 1b) are very similar to those in organic PCMs (Figure 1a). The difference is in the scale of values, in the case of samples in inorganic PCMs (Figure 1b), the CR values are much higher.



(A). Linpar 17 (organic PCM).



(B). Rubitherm SP25 (inorganic PCM).

FIGURE 1. Comparison of the dependence of *CR* value (in mg cm^{-2} year^{-1}) of metals in two types of PCMs.

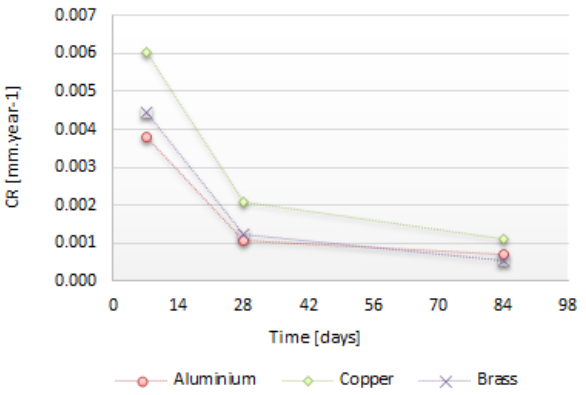
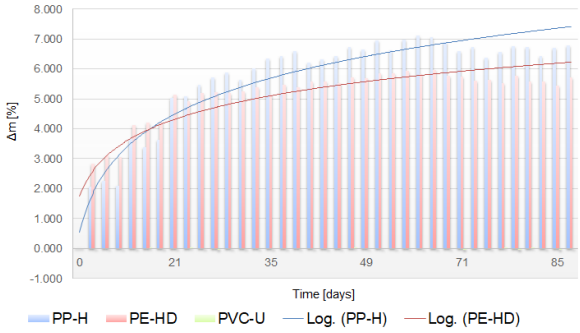


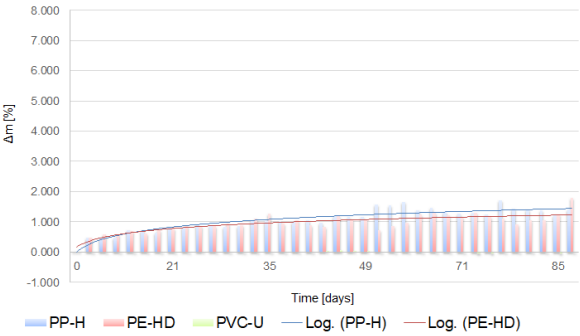
FIGURE 2. Comparison of the dependence of *CR* value (in mg year^{-1}) of metals in Rubitherm SP25 (inorganic PCM).

The *CR* parameters of the metal samples were compared with the limit values in The Guide for corrosion weight loss (in Table 3), unlike other study [2], all considered metal-PCM combinations can be classified as Recommended for long term service [8].

Figure 2 shows the *CR* values in mm · year^{-1} from which we determined the estimated service lifetime of these metal samples, which is 100 years for copper, up to 150 years for aluminium, and up to 200 years for brass when immersed in inorganic PCMs. This



(A). Linpar 1820 (organic PCM).



(B). Rubitherm SP22 (inorganic PCM).

FIGURE 3. Comparison of the dependence of Δm value (in %) of plastics in two types of PCMs.

evaluation will be complemented by a further experiment using the Planned Interval Test according to the methodology in ASTM [8].

The courses of the values of percentage change in mass of the samples are shown in Figure 3, it is a criterion for the evaluation of the mutual compatibility of the plastic-PCM pairs and the calculation is described in Section 2.2. The figures are presented for the representatives of the organic and inorganic PCM group as in the case of the metal samples. The results show that samples immersed in the organic group of PCMs achieved higher weight changes, where the maximum value of mass change reached 7 %. The organic PCMs have a higher ability to penetrate the matrix of the tested plastic samples, the penetration of organic PCMs into the plastics materials is demonstrated in Figure 3a. In terms of the selected materials, the smallest weight changes were found for PVC-U material and the highest for PP-H immersed in Linpar 1820 (organic PCMs), similar conclusions are described by Castellón [9]. All samples were checked after removal from the PCMs and no visual changes were observed on the sample surface, the same results are documented by Oró [2].

4. CONCLUSIONS

In this study, we focused on testing the compatibility of selected plastics and metals with organic and inorganic groups of PCM. According to the results presented in Section 3, a significant difference in the weight changes of the samples was found depending

on the selected group of PCMs. It was verified experimentally in the case of immersion of plastics in the inorganic group of PCMs, that less mass change and lower penetration of PCMs to the matrix of the tested samples occurred. The PVC-U samples did not show any significant weight changes, while a rapid penetration of PCMs into the samples of PP-H and PE-HD was clearly visible during the first 4 weeks, but this increase slowed down in the following weeks. The interaction between PCMs and metals was verified using the *CR* value. Compared to the plastics, the metal samples in the organic group of PCMs showed less weight and visual changes on their surface. The highest values were achieved in the case of the copper immersed in Rubitherm SP25, which is the worst variation of the metal-PCM pair in the experiment.

The test method for metals used in the experiment was based on the assumption of the normal (constant) corrosion rates during the exposure period of the metals in corrosive environments. In further research, we would focus on the testing metal-PCMs combination using the "Planned interval test". This method measures the variation of corrosion rates over time throughout the experiment.

Acknowledgements

This research was funded by Czech Science Foundation, grant number 19-20943S "Compatibility of plastics and metals with latent heat storage media for integration in buildings".

References

[1] ASTM G1–03 Standard practice for preparing, cleaning, and evaluating corrosion test speciments, ASTM International, West Conshohocken, PA, USA, 2019.

[2] E. Oró, L. Miró, C. Barreneche, et al. Corrosion of metal and polymer containers for use in PCM cold storage. *Applied Energy* **109**:449–453, 2013. https://doi.org/10.1016/j.apenergy.2012.10.049

[3] P. Moreno, L. Miró, A. Solé, et al. Corrosion of metal and metal alloy containers in contact with phase change materials (PCM) for potential heating and cooling applications. *Applied Energy* **125**:238–245, 2014. https://doi.org/10.1016/j.apenergy.2014.03.022

[4] G. Ferrer, A. Solé, C. Barreneche, et al. Corrosion of metal containers for use in PCM energy storage. *Renewable Energy* **76**:465–469, 2015. https://doi.org/10.1016/j.renene.2014.11.036

[5] A. J. Farrell, B. Norton, D. M. Kennedy. Corrosive effects of salt hydrate phase change materials used with aluminium and copper. *Journal of Materials Processing Technology* **175**(1):198–205, 2006. https://doi.org/10.1016/j.jmatprotec.2005.04.058

[6] P. Rolka, J. Karwacki, M. Jaworski. Compatibility tests between three commercially available organic PCMs and metals typically used in fin-and-tube heat exchangers. *Materials* **14**(18):5172, 2021. https://doi.org/10.3390/ma14185172

[7] ASTM G 31 Standard practise for laboratory immersion corrosion testing of metals, ASTM International, West Conshohocken, PA, USA, 1999.

[8] ISO 175:2010 Plastics – Methods of test for the determination of the effect of immersion in liquid chemicals. [2019-02-15]. https://www.iso.org/standard/55483.html

[9] C. Castellón, I. Martorell, L. F. Cabeza, et al. Compatibility of plastic with phase change materials (PCM). *International Journal of Energy Research* **35**(9):765–771, 2011. https://doi.org/10.1002/er.1723