

Article

Review and Analysis of Existing Approaches to Investigate Property Degradation of Phase Change Materials and Development of a New Systematic Approach

Harald Mehling 

Consultant (R&D), Weingartenstr. 37, 97072 Würzburg, Germany; harald.mehling@gmail.com

Abstract: With increasing commercial success of PCM, the long-term development of properties becomes more important. It has been investigated already for decades in a variety of ways and a wide range of testing conditions. Previous reviews concluded that further work toward standardization of testing is needed. In a desktop study, the current approach to testing was analyzed. It is shown that standardization should not mean to always test with the same methods using the same conditions, e.g., as different applications impose different conditions. Instead, testing should be tailored to the individual case. For this, a new, systematic approach was developed. It identifies first the basic functions and related properties that might be subject to testing, e.g., with a specific application in mind, and then gives an approach to find the degradation effects and underlying mechanisms to allow tailoring and optimizing test procedures. As an example, the approach is applied to the function of heat storage. Here, a new degradation effect was identified, and for degradation by phase separation, it is shown by an example that it could even be reversed at suitable conditions. Therefore, tailoring testing conditions to the individual case is needed. Deeper knowledge of degradation mechanisms is required, so further R&D is suggested.

Keywords: PCM; thermal energy; heat storage; property; degradation; ageing; stability; cycling; testing



Citation: Mehling, H. Review and Analysis of Existing Approaches to Investigate Property Degradation of Phase Change Materials and Development of a New Systematic Approach. *Appl. Sci.* **2023**, *13*, 8682. <https://doi.org/10.3390/app13158682>

Academic Editors: Ioannis Kartsonakis and Cesare Biserni

Received: 11 June 2023

Revised: 19 July 2023

Accepted: 21 July 2023

Published: 27 July 2023



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1. Introduction

1.1. PCM, PCM Composite Materials, and Encapsulated PCM

Due to the increasing use of renewable energy sources, specifically sun and wind, energy storage will play an even more crucial role in the future to be able to match availability of energy with demand. Thermal energy storage, often also called heat and cold storage depending on the type of application, has already today a significant share of energy storage. And its importance will further grow with increasing use of solar heat or heating or cooling by use of intermittent electricity from sun and wind.

Basically, three effects can be used for thermal energy storage: raising the temperature of a material as it is, changing its phase, or changing its composition. Just raising the temperature is the most frequently used, in technical applications as well as in everyday life. The associated heat is also called sensible heat because the temperature change associated with it can be sensed. For thermal energy storage, solids or liquids are used because gases store comparatively little thermal energy. When using a phase change, usually used is the phase change between solid and liquid, less often between different solid phases. In comparison to a phase change involving a gas phase, these not only allow storage of a significant amount of thermal energy in a small volume at low pressure but also in a narrow temperature range. If the phase change is even at a single temperature, the associated heat is called latent heat as it cannot be felt without temperature change. Materials able to store a significant amount of thermal energy, respectively, heat, when changing phase, are called Phase Change Materials (PCMs). It is also common to call them latent heat storage materials, even though many materials used as PCMs—e.g., many mixtures—change phase in a temperature range.

The ability to store a significant amount of heat in a small temperature range by using a phase change leads to two main fields of use [1]: heat storage with high storage density (per mass or volume) in a small temperature interval and passive temperature stabilization (temperature control). PCMs are today used in a wide range of commercial applications [2]: in buildings for space heating and cooling as well as for domestic hot water; in logistics, specifically in the cold chain; for heating or cooling the human body, including in medical applications, in mobility, in electronics; as well as in industrial processes. And more applications have been developed, e.g., for the energy system.

The most common PCM is water, with a solid–liquid phase change at 0 °C. For other temperatures, other materials must be used, like paraffins, fatty acids, alcohols, and salts, as a pure material or as a mixture, e.g., salt hydrates. Organic PCMs are also sometimes called bio-based if produced from biological sources. To work properly for thermal energy, respectively, for heat storage, many PCMs also contain additives, e.g., a nucleator to reduce supercooling or a gelling or thickening material to reduce phase separation. PCMs are also sometimes combined with other materials to combine material-specific advantages, thus becoming a PCM composite material. For example, PCMs are combined with graphite or metal foams, combining the ability of PCMs for heat storage and the ability of graphite or metal foams for heat transfer. Also, PCMs can be combined with polymer foams to give them a stable shape/form even if they are a liquid. In applications, encapsulated PCMs are often used to avoid loss of the PCM, specifically if it is a liquid, to avoid contact with the ambient, and to keep the shape/form as defined surface for heat exchange. Compared to a composite material where the PCM is combined with another material within its interior, in an encapsulation, the combination is with a material at the boundary, the PCM surface. Encapsulation also serves as a well-defined package size, and thus the encapsulated PCM acts as a heat storage module or object. Encapsulation sizes range from about 1 µm (called microencapsulation) to several 10 cm (called macroencapsulation), allowing PCMs to be pumped with heat transfer fluids (called slurries) or to be used in variable storage sizes. The shape and capsule wall material also vary, e.g., flat or ball-shaped containers from metals or plastic, or bags and pouches made from polymer foil.

1.2. Long-Term Performance

Besides the use of water/ice for cooling, specifically of food and beverages, the first use of PCM in a technical application was probably in the 1930s when M. Telkes investigated the use of PCM to store solar heat available during summer and use it for space heating in winter [3]. To store heat, containers with a large amount of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ as PCM, a salt hydrate called Glauber salt, were used. Already in the first year, a significant decrease in the performance of the heating system was observed. It was attributed to a decrease in the heat storage capability of the PCM with repeated phase change. Besides that, the metallic containers used showed leakage due to corrosion by the PCM contained. Not surprising, investigations on long-term performance have a long history after this memorable start. Leakage of PCM from containers due to corrosion is a matter of material compatibility, thus not a PCM-specific problem but rather a general topic of materials research—specifically, development and testing. Testing a combination of a PCM with another material is usually done by immersing a sample of the material in the PCM or by containing the PCM in a container with walls made of the other material. Testing is done at application-typical conditions—specifically regarding temperature and atmosphere—and sometimes including change of phase of the PCM but more commonly with the PCM in the liquid phase all the time. The understanding of mechanisms behind compatibility problems has increased in the past decades, as well as options to avoid them. Still, the variety of PCMs and materials used in contact with them for containment or heat exchange continues to make this a field with demand for more R&D. Investigations covering compatibility problems with salt hydrates and metals, or paraffins and plastics, are, e.g., described in [4–7], with the last one including a list of different studies. Compatibility is often tightly connected to leaking, such that leaking is avoided if a suitable material combination is found. For most cases, options

exist and just have to be identified. In contrast, the long-term performance of the PCM itself is more difficult. Testing the long-term performance of a PCM, specifically on full phase change, commonly called cycling, is usually done at application-typical conditions with regard to temperature and time, or just number of cycles. Typical causes of the poor cycling stability of a PCM are phase separation or the deactivation of nucleators. While the understanding of the mechanisms how nucleators work is still low, and also of their deactivation, a basic understanding of the mechanisms behind phase separation has existed for several decades already. While pure materials generally change phase between a liquid and a solid phase of same composition, mixtures of chemical compounds can form phases with different mixing ratio, so different composition. Consequently, the amount of material with correct composition and heat storage capability is reduced. If phases have different density, gravitation can lead to macroscopic separation, which is worsening the problem. Shallow containers, addition of materials for gelling or thickening, or mixing, can limit phase separation. While phase diagrams can be used to show the possible degree of phase separation [8], they cannot show the dynamics. So, preferred is to develop PCMs that have no risk of phase separation, which means PCMs that change phase between one single phase and another, just like pure materials.

But phase separation and deactivation of nucleators are not the only causes of a poor cycling stability. A high phase change enthalpy in a narrow temperature range is typical if the solid phase is crystalline, however, not if it is amorphous. For example, water in small amounts or if cooled fast can stay amorphous. For polymers, a volume fraction being generally amorphous is typical; it increases with the cooling rate. That a liquid phase changes to different crystal structures in the solid, depending on the conditions, is also possible, e.g., in erythritol [9]. Crucial is also if these effects are reversible. The formation of an amorphous or other crystalline phase in the solid is already reversible by melting. Reversibility of phase separation can depend on the specific conditions, or be impossible. More elementary is overall chemical change, e.g., if a salt hydrate absorbs water from the atmosphere. Similarly, oxygen from the atmosphere leads to a chemical reaction at high temperature in sugar alcohols [10,11]. The number of possibilities rises with new PCM material classes, with use of additives, or the development of shape-/form-stable PCMs and PCM composite materials.

Investigations of specific PCMs from many material classes, with a variety of methods, are numerous. Ref. [12] reviewed the methods previously used for “stability characterization” of PCMs. They state that this means the stability of thermal, chemical, and physical “properties”, after a number of repeated melting/freezing cycles, commonly also called cycling stability. They focused on four issues: equipment used to perform the cycling tests, techniques used to characterize the PCM before and after cycling and to check for “degradation”, the number of cycles performed, and the temperature–time profile used for the melting/freezing cycles. For these, they listed what has been used, and tried to find out a common, useful methodology. They concluded that no common standard for thermal cycling stability tests was available at the time. Recent updates were done by [13,14]. Summarizing, a PCM sample is placed in a temperature-controlled ambience, the temperature changing with time in a defined way. The temperature–time profiles used vary strongly regarding maximum and minimum temperature, the heating/cooling rate to reach them, and the time the temperature is kept constant, which define a single storage cycle, as well as number of cycles or time. Besides the temperature, other conditions are the exposure to gases, specifically air, N₂, Ar, or vacuum, and the container wall materials being glass, ceramic, metallic (aluminum, stainless steel), or plastic. While cycling is rarely done in a calorimeter due to cost and lack of flexibility of test conditions, differential scanning calorimeters (DSC) or other calorimeters are generally used to check the heat storage capability after a number of cycles. An indication of changes is mass change, even giving some hint on the reason of the change observed. Whether the mass of a sample has changed can be checked after a number of cycles. More detailed is, however, a separate measurement by thermo-gravimetric analysis (TGA), giving information on the temperature where the

change occurs. To find out potential causes of any change, information regarding structural changes often comes from X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), and also chromatography. An attempt to develop a methodology to test PCM candidates in R&D was published by [13], based on methods used by researchers to test new PCMs. But testing commercial PCMs differs, specifically if for quality assurance. Here, minimum quality requirements are needed, defining when a product fails specifications. An analysis of reasons for failure is not needed, quite contrary to R&D. In 2004, several companies founded the RAL Quality Association PCM to develop such minimum performance requirements and suitable procedures for quality assurance of commercial PCM products. These Quality and Testing Specifications for PCM (RAL-GZ 896) were published in 2006 in the 1st edition, later updated [15,16], and contain information on issues discussed here.

What is the current state? PCMs are generally characterized regarding their heat storage capability, sometimes their thermal conductivity (specifically if enhanced), sometimes their viscosity (in slurries), and their compatibility, specifically with regard to corrosion. Long-term performance is tested usually by cycling, meaning repeated phase change, but for compatibility, then usually just in the liquid phase. Long-term performance, e.g., in building applications at application-typical conditions, can be time consuming, so accelerated testing has been discussed generally and at some depth by [13]. However, most of the discussion is on what is tested and how. Ref. [14] concluded that, considering the diversity of the used devices and the wide range of experimental parameters, further work toward a standardization of PCM stability testing is needed. Then, what are the key questions?

The key questions are as follows: what should be tested, how should it be tested, and as a basis, why should it be done that way. In this paper, a “systematic approach to investigate property degradation” is presented by selecting suitable terms, classifying approaches for testing, finding the properties to be tested, giving an approach to identify degradation effects and underlying mechanisms, and applying it to the most crucial function: heat storage.

2. Materials and Methods

This study is carried out with respect to PCM in general, not specific to any material class, etc.

The method used is a desktop study. It is based on about 20 years of experience of the author in the area of PCM characterization, testing long-term performance, and quality control, as well as the work of others published in the available literature.

3. Results

3.1. Development of a General Systematic Approach

3.1.1. Selection of Suitable Fundamental Terms

A systematic approach needs suitable terms, being summarized in Figure 1, and later discussed in detail. Some of them, specifically “property”, “degradation”, and “condition”, are somewhat established in the field. However, they are not used by all authors, and sometimes even various terms are used in a single publication. Those terms marked in red in Figure 1 are new, introduced here to allow a comprehensive discussion of the topic.

PCMs, PCM composite materials, and encapsulated PCMs have “functions” regarding their application, each function being described by a physical or chemical “property”. E.g., the function for heat storage can be described by the physical property enthalpy. The value of the property can change during use in an application. If the property change is in an unfavorable way for the application, this is called “degradation”. A change is caused by a “degradation effect”, e.g., phase separation, due to an underlying “mechanism”, like the formation of phases with different densities and their macroscopic separation by gravity. Degradation is affected by “conditions” during use, as they affect the chemical or physical mechanism. First is the temperature, automatically related to the number of storage cycles or time (possibly also without changing phase). Then come other conditions, like the

exposure to forces (external pressure, gravitation, internal forces by thermal expansion, etc.) and exposure to other substances (gases, walls, etc.).

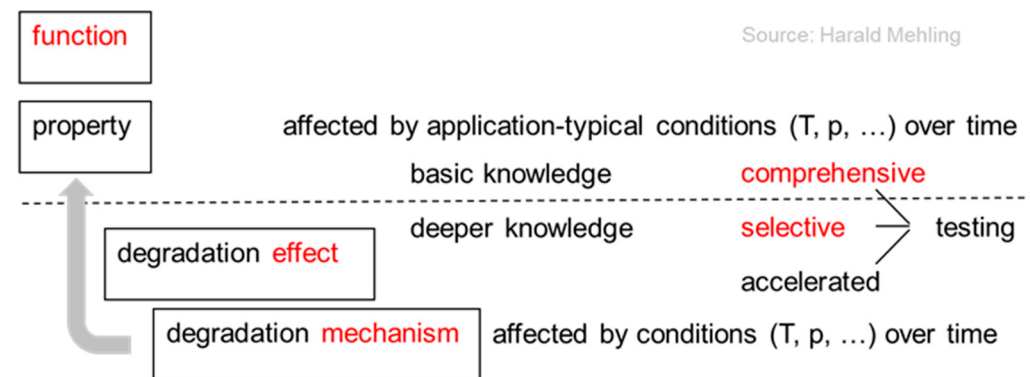


Figure 1. Overview on fundamental terms and relation to testing.

Various terms are in use specifically to discuss the crucial “property change” during use in applications such as stability, aging, or degradation [14], with reference to a property, performance, etc. For a scientific-technical discussion, including specifically quality control, not all of them are useful. The term “performance” refers to a specific situation and action. It has no measurable value in general; the performance with respect to a required function is good or bad, or sufficient, etc. It is therefore not useful in a scientific-technical discussion. In contrast, a physical or chemical property has a value, for example, the enthalpy change in J/g, or the thermal conductivity in W/(m·K). Consequently, physical and chemical properties allow a quantitative and not just a qualitative discussion. “Aging”, from its meaning refers to an effect with time; even more crucial is it has no measurable value. “Stability” is a term that expresses the optimum performance, but also has no quantitative, measurable value to describe changes. But it can be used with a “yes” or “no” answer regarding positive expectations. This makes it suitable for quality control on a customer level. Quality means a promised function is observed in reality with sufficient stability during use, so a “yes” answer on stability means a promised function is observed within guaranteed limits, while “no” means that the function is not as was promised. More suitable, and established for product testing [17], is the term “failure”. “Failure” is defined by the property changing to values not within specified limits for customer use, so it is measurable. The quality criteria at PCM-RAL [16] define a specific value at which, due to degradation, a product fails specifications. This is crucial if producers guarantee a value of a property for a product. The term “property degradation” therefore seems to be the most suitable for scientific-technical discussions, including discussing quality control in a scientific-technical context. Property degradation refers to a measurable value, specifically of a physical or a chemical property, and expresses that it refers to a possible negative trend. So, for the discussion here, the term “property degradation” is used throughout. The fundamental terms are now introduced (and suitable and unsuitable ones discussed with explanation).

3.1.2. Classification of Approaches for Testing and Identification of Optimization Potential

An analysis of what is done for testing shows that basically three approaches can be distinguished (Figure 1). As they are crucial for a systematic approach, and to understand why testing is done the way it is done, an attempt is made to explain and define them here.

Various aspects are relevant for testing. First of all, what is tested, why it is tested, and what is the focus. For example, a whole system can be tested (maybe for air-conditioning) that includes an ice storage, or just the ice storage, or one macroencapsulation with ice as a component of it, or just the ice as PCM. The focus can be one or several functions, for example, a PCM-graphite composite is used for heat storage, but as a composite with graphite, specifically if used for higher thermal conductivity, also for heat transfer. The

property that describes the function, for example, the enthalpy $h(T)$ that is describing heat storage, is investigated with one or several conditions in mind, specifically temperature. If there is a specific application in mind on testing or not strongly affects the focus chosen for testing. For example, if testing an air-conditioning system, application-typical conditions can be used for testing, like typical room temperatures and outside temperatures, thus a range of values, but also extreme values. Also, with an application in mind, typical lifetimes and/or number of usages are expected and tested. If testing is for R&D or for quality control, so for degradation of a property value or for failure (meaning that a property value fails at given specification), is also crucial. Is there interest to know degradation effects, maybe also underlying mechanisms, such that an analysis is of interest beyond just the plain testing? And related to that, is there previous knowledge? For example, in R&D, it is often known what is tested, while in quality control of a product, usually its construction and composition are largely unknown.

The most comprehensive testing would be testing with respect to all functions of what is to be tested, with regard to all conditions, their possible variations including extreme limits, and for full required lifetime, respectively, the number of usages or until failure. Having an application in mind, the application already reduces the variations significantly from the beginning. For example, a transport box with PCM to stabilize the temperature typically has a specific application case, for example, the transport of vaccines, world-wide, up to a week. The function is clear, the conditions of use too, and testing for typical lifetime including at extreme conditions is feasible. So, comprehensive testing is possible, and usually it is done. The reason that comprehensive testing is possible is because the application already limits variations. Knowing, e.g., the type of PCM is not necessary at all for testing. Testing a new PCM for transport boxes can, however, be different. If no information on the PCM is available, it should be tested comprehensively. But if the PCM to be tested is known to be a pure substance, then testing for phase segregation isn't needed. Or if the PCM is water, then thermal decomposition at typical application temperatures is impossible. Therefore, with increasing knowledge on what is to be tested and why, e.g., for which application, it is possible to limit the functions to be tested to those known to be crucial, and knowing the possible as well as impossible degradation effects, the number of conditions and range of their values including extremes can also be limited to those being crucial. Effort and time required for testing all variations is excessive. Therefore, selective testing, by selecting the functions and conditions on testing, saves effort and also time. However, limiting variations by an additional selection is at the risk of missing something crucial. Even doing comprehensive testing if the variations to be tested are given by an application has a risk. Already what exactly is application-typical? Cycling requires a repeated temperature change with time. If the property to be tested has a degradation mechanism significantly affected by temperature or time, then what is application-typical? A temperature–time profile with a step? Or one with a linearly increasing ramp? These questions show that selective testing should be avoided without additional, deeper knowledge.

Deeper knowledge, about degradation effects, underlying mechanisms, and conditions affecting them, is crucial for selective testing. A common and very important example is the function of heat storage, described by the property-specific enthalpy, and focus on the degradation mechanism of phase separation. The critical condition is temperature, specifically the temperature range where the PCM isn't fully solid. To reduce the effort, one can follow 3 steps: (1) Could degradation happen at all? If no, then why test? If yes, then (2) Does degradation happen (qualitative question) at the given conditions? If no, then stop. If yes, then (3) How much degradation (quantitative question) does happen? If the PCM used is known to be a single chemical compound, e.g., water, highly pure, degradation of the phase change enthalpy by phase separation cannot happen at all. Temperature is then not a critical condition, so why test its effect? If the PCM is known to be a salt hydrate, degradation by phase separation could happen. Then, does degradation happen? Phase separation in a salt hydrate is only possible in the liquid phase. Temperatures where

the PCM is solid are not relevant and can therefore be eliminated from testing, at least for a first, qualitative answer. The PCM could be kept liquid at constant temperature above the phase change temperature, for longer than a typical cycle, to check if different phases separated from each other occur. If phase separation is observed, then afterwards, cycling under a variety of temperatures and temperature–time profiles can be performed at last. The detailed investigation, with the biggest effort, is now only performed if it is required, as the last step. In the example, in the 1st step, a prediction is done, requiring theoretical knowledge or a phase diagram. In the 2nd step, the experimental effort is reduced and the sensitivity of testing increased by not cycling at all, requiring theoretical knowledge on mechanisms behind the individual degradation effect. If a PCM might decompose at high temperatures, it is similarly possible to select first a temperature higher than in its application for testing, and if no decomposition is observed, testing under application-typical conditions, meaning cycling, is not needed. This is commonly done by TGA, scanning a large temperature range in a single, continuous heating test.

Generally, to limit the effort and the time of testing, the functions looked at and conditions investigated and their variations are selected based on interest and on experience of what is important and/or critical. This is why generally the heat storage capacity is investigated, sometimes thermal conductivity, compatibility, leakage, etc.; why typically the sample is subject to repeated phase change (called cycling), sometimes substances the sample is in contact with, etc.; and why a fixed $T(t)$ profile is used for cycling. Without thinking much about it, all real testing is already a selection, automatically done, often unaware. This explains why the reviews on the used testing methods [12–14] show an overwhelming majority of testing PCMs under cycling and checking for changes in the heat storage capability, typically phase change enthalpy and temperature, e.g., by DSC. And it also explains why cycling is performed in a wide variety of individual ways; without defining a specific application, there cannot be an agreement on application-typical conditions to be used for testing. However, often cycling is also done simply the way the equipment allows, sometimes even done just as fast as possible to save time.

The analysis thus shows that standardization of testing should not mean to try to define testing in a way that testing is always done with the same methods at the same conditions. This is not applicable as already different applications impose different conditions. But it is also not possible to test everything for reasons of time and experimental effort. Therefore, it is clear that testing should be tailored to the individual case. As the analysis has shown, this is already done in some aspects, however not systematically. Therefore, here, a systematic approach to tailor and optimize testing is developed. The following sections identify first the basic functions and related properties that might be subject to testing, e.g., selected with a specific application in mind (Section 3.1.3), and then an approach is given to find the possible degradation effects and underlying mechanisms to allow tailoring and optimizing test procedures (Section 3.1.4). Before, however, another reason why the degradation effects and mechanisms must be studied in more detail related to testing is discussed for completeness.

Selective testing reduces the number of variations that need to be tested, but this is not always sufficient. For example, a PCM in a building application is supposed to be used for 10, 20, maybe even 30 years. For testing a final product at application-typical conditions, several months, maybe even four seasons, might be accepted. But during development, testing again at various development steps, a month is long. Even to test a single set of conditions, the available test time is a fraction of the application-typical time. The easiest approach is then to observe degradation within the available test time and then extrapolate, e.g., to full life-time, life-usages (like phase changes), sometimes even calculate rates. Figure 2 shows five measured data points (black) within test time and extrapolation assuming a linear correlation. A linear correlation, thus degradation at constant rate, is commonly used in corrosion as the corrosion rate. A disadvantage of extrapolation is not knowing if it is justified, e.g., it is not justified in corrosion if there is passivation.

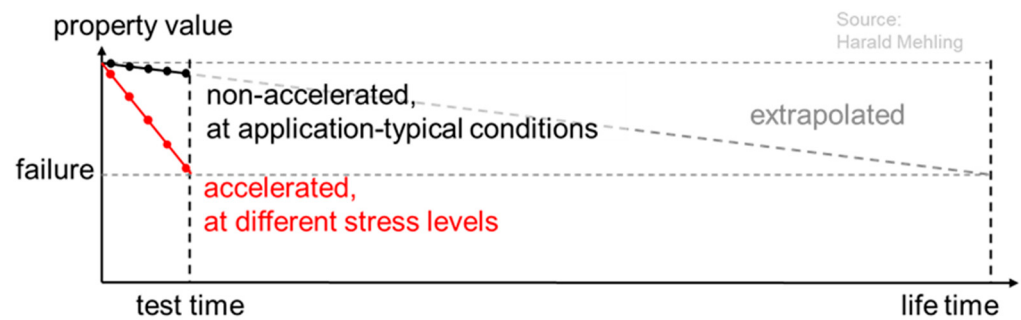


Figure 2. Property degradation data from tests, extrapolated beyond test time, and from accelerated testing.

Degradation might be accelerated by applying conditions outside application-typical conditions, e.g., higher temperatures. Conditions that accelerate degradation are called “acceleration factor”. By testing outside application-typical conditions, an attempt can be made to increase the “stress” and thereby accelerate degradation (Figure 2, red data points), in turn shortening the test time compared to application-typical conditions. Tested is degradation versus time, at different values of conditions, e.g., different temperatures. The correlation between observed times and values of conditions, described by a function, allows one to derive degradation times at application-typical conditions, so non-accelerated, from those observed when accelerated by a change in conditions. Thus, the correlation allows estimates for degradation at application-typical conditions in shorter test times.

Accelerated testing is “accelerated degradation testing” or “accelerated life testing” [17]. In the last one, specifically the life time is observed, with end-of-life defined by “failure”, meaning a property failing specification. Often the function describing the observed correlation, which is also called “lifetime-relationship model”, is just an empirical fit to observed data, used without scientific basis. However, ideally the function should be based on a “physical or chemical model” for the “mechanism” behind it (e.g., Arrhenius model). A good example is again the function of heat storage, described by the property of specific enthalpy, and focus on a degradation mechanism by temperature. Let’s assume a PCM has an application-typical number of 1000 cycles; too long to test. And let’s look at a degradation by 10%, so to 90% of the initial value. The observation could be for testing at 20 °C above application-typical temperature that a degradation by 10% is observed after 10 cycles, at 10 °C above after 50 cycles, and at 5 °C above after 100 cycles. The data show a correlation between testing temperature (condition varied) and number of cycles, which can be used to predict the number of cycles where 10% degradation is observed at 0 °C above and thus at application-typical temperatures, now without testing as many cycles. Ref. [13] discuss accelerated testing in detail, including as an example the thermal degradation of D-Mannitol, with graphical evaluation. As before, accelerated testing also requires deeper knowledge: a suitable degradation factor and whether different conditions and degradation effects might affect each other.

The following sections identify first the basic functions and related properties that might be subject to testing, e.g., selected with a specific application in mind (Section 3.1.3), and then an approach is given to find the possible degradation effects and underlying mechanisms to allow tailoring and optimizing test procedures (Section 3.1.4). This is done systematically, analyzing knowledge on PCM application and testing as well as basic knowledge from Physics and Chemistry.

3.1.3. Selection of the Basic Functions and Corresponding Properties

The literature reviews [12–14] have identified many things that are commonly tested. Looking specifically at PCMs, PCM composite materials, and encapsulated PCMs, they are tested for their phase change enthalpy, temperature, density, mass loss, thermal conductivity, viscosity, compatibility, corrosivity, leakage, etc. Each “function” of a PCM, PCM

composite material, or encapsulated PCM in a heat storage application should be subject to testing, so described by a “property” (Figure 1). What is the systematics behind here?

The crucial, basic functions in an application are heat storage and, related, the needed heat transfer (Table 1). The function of “heat storage” can be described by the specific enthalpy $h(T)$ with regard to mass m or volume V for materials, such as for PCM and PCM composite materials. Encapsulated PCMs are not materials but objects; heat storage is here described by the enthalpy H of a single object, so of a single capsule. The “heat transfer” is described by the thermal conductivity λ for PCMs and PCM composite materials. For encapsulated PCM’s heat transfer is not described by the thermal conductivity; actually, it cannot be described by a single property. Instead, heat transfer depends on a set of properties, including the thermal conductivity of the PCM and capsule wall, and the shape/form and surface area of the encapsulation.

Table 1. Basic functions of PCM, PCM composite materials, and encapsulated PCM in applications for heat storage and their corresponding physical or chemical properties for description.

Basic Function	Thermal		Mechanical	Protecting Functions. . .	
	Heat Storage	Heat Transfer	Keep the Shape/Flow	Protecting the PCM	Protecting the Ambient
PCM	$h(T)$	λ	$E, \eta, \dots$	$m/V, \dots$	$m/V, \dots$
PCM composite m.	$h(T)$	λ	$E, \eta, \dots$	$m/V, \dots$	$m/V, \dots$
encapsulated PCM	$H(T)$	λ, A, shape	$E, \dots$	$m, \dots$	$m, \dots$

The more technical functions and corresponding properties are not so obvious, despite how they seem at first. Encapsulations have several functions: to avoid loss of the PCM, specifically liquid phase flowing away, to avoid contact with the ambient, and to keep the shape/form (specifically rigid encapsulations). But avoiding loss and contact are not basic functions with respect to applications. Basic functions are regarding heat and mass transfer, specifically to keep the shape for heat transfer, e.g., using rigid encapsulations, and the flow behavior for mass transfer, e.g., in liquid slurries, and additionally, specifically to protect from degradation and related issues, protecting the PCM from the ambient as well as protecting the ambient from the PCM. “Protection of the PCM” comprises avoiding loss of PCM, and avoiding changes in its composition by contact with the ambient, e.g., by taking up or losing water. “Protection of the ambient” means avoiding contact to the PCM, e.g., due to leakage. And both also contain compatibility, e.g., corrosivity. The function to “keep the shape” is described by the modulus of elasticity E for shape-stabilized or encapsulated PCM, and the function “flow” by the viscosity η for PCM slurries. The function “protecting the PCM” must be described depending on the situation: regarding loss of PCM, it can be described by the PCM “mass loss” to the ambient, regarding uptake of harmful substances from the ambient by the “mass uptake” and its specific effect (e.g., water uptake).

If necessary, more functions can be added to thermal and mechanical ones, e.g., electrical functions for the case of battery thermal management, specifically the electric conductivity, or optical functions for daylighting modules [18], like the optical transmittance. Further on, other properties can be specified, e.g., with regard to protecting the environment, properties describing safety risks.

To tailor testing to the specific case, e.g., with an application in mind, it is now possible to select the basic functions and related properties which are relevant to test from this systematic overview.

3.1.4. Approach to Identify Degradation Effects and Underlying Mechanisms

Having decided on the functions and related properties to be tested in an individual case is, however, only the easy part. To tailor testing of the selected properties afterwards to what is important/critical is much more complicated, specifically with regard to the selection of the test conditions. As a first step, however, always the relevant degradation

effects and underlying mechanisms with regard to the property must be identified. A systematic approach to find them is now given.

Each function is described by at least one corresponding physical or chemical property (Figure 1, Table 1) to be measurable when testing, for example, the property enthalpy describes the function of heat storage. Degradation of a property can be due to different degradation effects, e.g., the enthalpy can degrade due to phase separation, nucleator deactivation, or thermal decomposition, or possibly more than one act. The mechanisms underlying the degradation effects are affected by the conditions, e.g., the temperature. For example, the temperature can cause the formation of different phases and nucleator deactivation, both leading to a degradation of the enthalpy. At the same time, temperature also affects other properties. Selective testing, which focuses on selected properties and conditions, often a range of values of a single condition, requires deeper knowledge about the PCM, PCM composite material, or encapsulated PCM to be tested, specifically possible degradation effects, underlying mechanisms, and how conditions affect them. Besides testing an application at application-typical conditions, basically all real testing is done for a selection. Without knowledge, a selection means to risk missing what is critical, or wasting time on testing the obvious. Accelerated testing, e.g., investigating the enthalpy when cycling at a temperature–time profile which is not application-typical to accelerate degradation and finally to make predictions for application-typical conditions, requires identifying an acceleration factor, meaning a critical condition, sometimes more. Deeper knowledge, meaning understanding properties, degradation effects, and mechanisms behind them, is needed.

To identify possible degradation effects and underlying mechanisms, a systematic approach can, e.g., be checking from the small, the atomic, and molecular levels to the large levels, like external surfaces (Figure 3). Different functions, as being described by physical and chemical properties, are based on underlying structures, like bonds between atoms, crystals, etc. That properties are often connected is thus no surprise. The approach in Figure 3 is useful for the function of heat storage, as the discussion in Section 3.2 will show. It is also useful for the function of heat transfer as well as mechanical ones to keep the shape and flow. However, Figure 3 seems not useful for compatibility issues, like corrosion. Nevertheless, as it is the common systematic way to think of materials in physics, chemistry, and engineering, the presented approach should be useful, maybe with some modification, for most properties and their degradation.

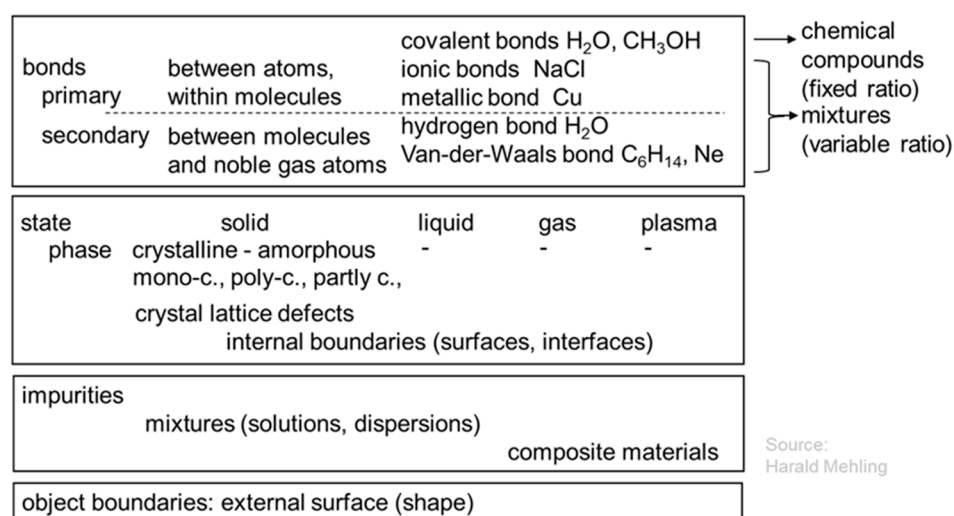


Figure 3. Systematic approach to analyze materials and changes in materials.

The general systematic approach developed in Section 3.1 comprises the approaches for testing, the basic functions, the corresponding properties to test, and an approach of how

to identify degradation effects and underlying mechanisms. It is now used in Section 3.2 to develop a detailed approach for the example of the most crucial function: heat storage.

3.2. Development of a Detailed Systematic Approach for the Function of Heat Storage

A detailed, systematic approach must cover the basics of the related property, how it can be measured, the related property values and their uncertainty, the systematic identification of the possible degradation effects and underlying mechanisms, and testing.

3.2.1. Property Basics and Related Property Measurement

The behavior of a PCM can differ significantly from the ideal case with a phase change temperature T_{pc} . A PCM can show a phase change temperature range (Figure 4), even behave differently upon heating and cooling, called hysteresis. A case of hysteresis is if upon cooling the new phase is not formed until a sufficiently low temperature, the nucleation temperature T_{nuc} , is reached. This is called subcooling, supercooling, or undercooling, and depends on the sample size, cooling rate, and (if any is used) the nucleator.

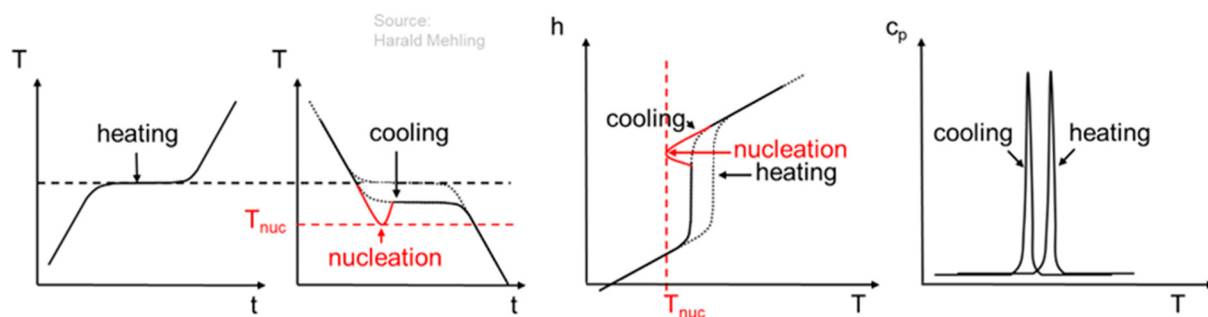


Figure 4. Phase change with a phase change temperature range and hysteresis incl. supercooling.

Phase change temperature T_{pc} and enthalpy change $\Delta_{pc}h$ are thus not sufficient data to characterize heat storage. Proper characterization of a PCM is done using heating and cooling curves of the specific enthalpy $h(T)$, typically mass or volume-specific values, e.g., in J/g or J/cm³, and the sample-size-dependent nucleation temperature T_{nuc} . The same applies to a PCM composite material. Encapsulated PCMs are individual objects, thus the description is done by an object-specific enthalpy, e.g., in J, and object-specific nucleation temperature.

Methods to determine the heat stored are called calorimetric methods. Commonly used for PCMs are differential scanning calorimetry (DSC), T-history, 3-layer calorimetry, or modified heat flow meters [16]. For composite materials, being by nature inhomogeneous, methods with sufficient sample size to be representative have to be used. An encapsulated PCM is not a material but instead it is an object; therefore, calorimetric measurements must be done on it as a whole, e.g., on a whole pouch. Ideally, measurements give a resolution better than 1 °C. When doing a calorimetric measurement, the heat flux into or out of a sample is associated inevitably with a heat flux within it, and therefore an internal temperature gradient. Because of this temperature gradient, heat exchanged by the sample can only be attributed to a sample temperature within some temperature range. This effect, always present, increases with the heating/cooling rate as well as sample mass and its dimensions [19]. For PCMs, when changing phase the effect is already relevant even in small samples, so even for DSC measurements on small samples, a small heating rate has to be chosen for a good temperature resolution. PCM composite materials must be measured on samples large enough to be representative for inhomogeneities of the composite, so typically larger than for PCM, so this effect is hard to keep small. And for large, encapsulated PCMs, good temperature resolution is often impossible to get at acceptable effort. It is then common to use calorimetric methods which give no temperature resolution at all but are simple. The simplest setup, and extremely flexible regarding the sample size and shape, is a mixing calorimeter. In a mixing calorimeter, the sample

exchanges heat with a reference liquid, and the heat stored by the sample between initial and final temperature is calculated from the same for the reference liquid [20–22].

3.2.2. Degradation Effects and Underlying Mechanisms

Knowing the basics of the “property” enthalpy, which is used to describe the “function” heat storage, the next thing to do is to generally analyze the “degradation effects” and their underlying “mechanisms”. For a specific case, e.g., for a specific PCM, this will allow looking for possible degradation mechanisms, and answer the question if degradation could happen at all. Further on, it allows drawing conclusions on the selection of test conditions, e.g., the $T(t)$ profile during cycling. Currently, knowledge of degradation effects and mechanisms is from experience for specific material classes, like phase separation for salt hydrates, oxidation of organic PCMs, compatibility of salt hydrates and metals or organic PCMs and plastics, etc. However, if a new material class is investigated in search for new PCM, then there is no previous experience. And even if a material class is already investigated for a long time, are the known degradation effects and underlying degradation mechanisms complete? Is it possible that when selecting specific effects, mechanisms, or conditions for selective testing we miss something? A systematic approach is needed. It is now developed, using the approach described in Section 3.1.4, Figure 3. The results are summarized in Table 2.

Table 2. Degradation effects and underlying degradation mechanisms for the function “heat storage”.

Degradation Effect	Underlying Degradation Mechanism
change in the chemical composition of PCM to other chem. compounds (atomic/molecular level)	chemical reaction, e.g., decomposition of just the PCM, or a reaction of the PCM with a substance it is exposed to (a compatibility issue, after failed protection of the PCM)
change in the chemical composition of PCM from a mixture to others on a small distance	unmixing of a mixture on cooling and microscopic separation, e.g., eutectic mixtures solidifying after supercooling, or change in the mixing ratio by exchange of matter with the ambient (a compatibility issue, after failed protection of the PCM)
change in the chemical composition of PCM from a mixture by unmixing on a larger distance (called phase separation or phase segregation)	formation of more than a single phase, with different densities, and macroscopic separation by gravity to a relevant degree (thermal diffusion or mixing not sufficiently present, and the same for gelling or thickening materials in PCM composites)
change in the physical composition of the PCM, specifically the low temperature phase at crystal scale, to one that is not wanted	formation of a crystalline phase not wanted (polymorphism), or even an amorphous phase, in whole or in parts (e.g., PE, water, salt hydrates, salt-water eutectics, if not given sufficient time for crystallization upon fast cooling)
no or late (called supercooling), or early formation of the desired low-temperature phase of the PCM	no, or late, nucleation of the desired low temperature phase, e.g., due to a deactivated nucleator or inhibited crystal growth, or early nucleation if stable supercooling is desired

Basically, a PCM is a single chemical compound or a mixture of several chemical compounds. For heat storage, the PCM undergoes a change in phase, meaning of the chemical composition and/or physical composition, the latter referring specifically to its crystal structure, crystallinity, and other related things. This is also the origin of the phase change enthalpy $h(T)$, being the basis for the function of heat storage.

The first degradation effect is a change in the chemical composition of the PCM to other chemical compounds, thus at the atomic/molecular level, and the related degradation mechanism is then a chemical reaction. The simplest example is a decomposition of just the PCM. For example, normal paraffins are known to undergo thermal decomposition to methane and the corresponding olefine [23]. At ambient atmosphere, normal paraffins react with oxygen, forming fatty acids, starting at about 150 °C [24]. Erythritol was also investigated with regard to this effect [25]. The exposure to another substance, like oxygen, is an issue of compatibility, and thus protection of the PCM.

The next degradation effect is a change in the chemical composition of the PCM a level beyond molecules (so at the same chemical compounds), possible if a PCM is a mixture of compounds, from an initial composition to another. In metallurgy, the effect and underlying mechanism is well known. As described by [26], an alloy of 35 wt.% Co–65 wt.% Ni, a binary isomorphous system, forms different microstructures at equilibrium and at non-equilibrium solidification. At non-equilibrium solidification, solid phases with locally different concentrations form because mass diffusion is too slow to result in a homogeneous mixture of the same concentration throughout the whole volume. It is important to note that this effect, resulting from non-equilibrium, is not indicated by phase diagrams, as they describe equilibrium states. For PCM, Ref. [27] investigated tetradecane and hexadecane mixtures and also classified them as a binary isomorphous system. Using DSC, Ref. [27] found that the mixtures melt and freeze over a temperature range, and specifically that the temperature range depends on the DSC ramp rate. They concluded that the behavior of binary mixtures of n-alkanes is far more complicated than considered in earlier studies. Similarly, eutectic mixtures solidify without supercooling into two different mixtures, at the same time, separated only by a very small distance. However, if there is supercooling, meaning a non-equilibrium, the mixing ratios could change further, at small distances, and consequently also the overall heat stored. In both cases, complete melting brings back the initial state, thus eliminating any previous degradation. The crucial question remains what happens if binary isomorphous mixtures are not melted completely. The mixing ratio can also change by the exchange of matter with the ambient. Then the mechanism is again a compatibility issue, after failed protection of the PCM. e.g., salt hydrates can change the mixing ratio by water exchange with the ambient, and as long as the changes remain small, like an impurity, this might not have consequences beyond the mixing ratio on short distances.

The next degradation effect is a change in the chemical composition of the PCM from a single mixture to more than one, as before, but now followed by unmixing on a larger distance, called phase separation or segregation. The underlying degradation mechanism is a formation of more than one phase with different mixing ratios, different densities, and the successive separation by gravity or centrifugal forces. This requires, different than before, that at least one phase is liquid to allow separation on a larger distance. Phase separation is a complex effect because the underlying mechanism depends on a series of steps: first, the formation of phases of different densities, then their macroscopic separation and lack of effective opposing mechanisms like thermal diffusion or mixing and limiting measures like gelling or thickening. Phase separation is commonly discussed using phase diagrams, which show if a PCM changes phase in a congruent, semi-congruent, or incongruent way. Congruent melting occurs if all liquid and solid phases have the same composition [8]; this means that for congruent melting already the initial step needed for phase separation cannot happen. However, knowledge of what happens in all the other cases, and the consequences for heat storage, is still far from being sufficient. Phase separation can occur if phases of different densities form and if at least one of them is liquid to allow motion on a large distance. However, already phase diagrams show that in many cases just heating to a temperature somewhat above phase change leads to remixing, in equilibrium, if only sufficient time is given for the process to happen. What “sufficient” time means depends on the effectiveness of remixing, by thermal diffusion or by free or forced convection (mixing), and the distance that phases have separated, limited by the height of the container or encapsulation or further limiting measures like the use of foams, gelling, or thickening. Phase diagrams show if phase separation can happen. But phase separation is not a problem by itself. Crucial is if separation accumulates to a degree that significantly reduces the heat storage capability, thus how far degradation proceeds. Actually, in ice slurry generation from brines, phase separation is even used intentionally.

All options regarding a change of the chemical composition of a PCM, being a single chemical compound or a mixture of more than one chemical compound, have now been treated: first the change to other chemical compounds, possible in pure substances as

well as in mixtures, then, for mixtures, the change to other mixtures without large distance separation, and then also with large distance separation. The physical composition is the arrangement of the atoms/molecules at a given chemical composition. Physical composition thus refers to the crystal fraction, called crystallinity, and the specific crystal structure. A change in phase generally means a change in the chemical composition and/or physical composition. For heat storage, a PCM undergoes preferably a change in the physical structure, not the chemical one. The change in the motion and in the position of atoms/molecules between the phases of a phase change determines the enthalpy change $\Delta_{pc}H$ as well as the entropy change $\Delta_{pc}S$. At equilibrium between phases, both are related by $\Delta_{pc}H = T_{pc} \cdot \Delta_{pc}S$, and consequently, they determine the phase change temperature T_{pc} . How much heat is stored, given by the phase change enthalpy, increases with entropy change. For this reason, the low-temperature, solid phase should be crystalline, because crystals have low entropy due to their regular arrangement of atoms/molecules. This leads to two further degradation effects.

The next degradation effect is thus a change in the physical composition of the PCM on the crystal scale, specifically with regard to the low temperature phase, by formation of a phase that is not the one wanted. The underlying degradation mechanism is the formation of another crystalline phase or even a phase which is not crystalline, thus amorphous (e.g., PE, supercooled water, salt hydrates, or salt-water eutectics). The existence of several crystalline phases is called polymorphism, and a known reason for degradation (e.g., observed for d-Mannitol by [28] or tristearin [29]).

A second possible degradation effect regarding the change in the physical composition is no, late, or early formation of the desired low-temperature phase of the PCM. e.g., for solid-liquid phase change, the high-temperature, liquid phase could cool below the phase change temperature without phase change, and thus stay in the high-temperature, liquid phase. The underlying degradation mechanism is commonly a failure of nucleation of the low-temperature phase and rarely that nucleation works but crystal growth fails. If a nucleator, a substance which should cause nucleation, was added to the PCM, degradation could be due to deactivation of the nucleator, possibly by temperature or also by substances that cover its surface. Nucleation can still happen via the PCM, but then typically later than if the nucleator would be active. Also, if stable supercooling is desired in an application for long-term heat storage with less heat loss, too early nucleation is also a kind of property degradation.

The previously discussed degradation effects cover the composition of the PCM from the small to the large scale. Further on, the systematic approach assures that the described effects cover all possible basic effects.

3.2.3. Testing of Degradation

For an individual case, based on the selected property to be tested and knowing the possible degradation effects, final decisions on the test design can be made. Testing can be done with regard to a specific degradation effect or be general such that the possible degradation effects help to understand observations. This is largely a matter of the interest and goal of testing. In any case, it must be kept in mind that the selected conditions (T , p , etc.) affect the result of degradation testing.

For the function of heat storage, described by the property enthalpy $h(T)$ on heating and cooling (covering the full phase change), testing is generally done by calorimetric methods. Further on, besides the $T(t)$ profile used for the calorimetric measurement, the sample is of course exposed to a $T(t)$ profile for testing degradation with time (e.g., called cycling). It is technically possible to do both in the calorimeter, and for many reasons, the exposure to a $T(t)$ profile for testing degradation is however commonly in an individual setup.

The most common way of testing is simply testing under application-typical conditions for degradation and only determining the property enthalpy in well-defined intervals, for example, after every 100 cycles. However, as discussed before, what is application-typical?

And where are the limits of the conditions where degradation starts? And without deeper understanding, accelerated testing is also not possible. Thus, a deeper knowledge (Figure 1) of the degradation effects, the degradation mechanisms behind them, and the conditions affecting them is needed. These issues are now briefly addressed with regard to the two most commonly investigated degradation effects: changes in the chemical composition of a PCM to other chemical compounds and changes in the chemical composition of a PCM from a mixture by unmixing on a larger distance (called phase separation or phase segregation).

A change in the chemical composition of a PCM to other chemical compounds by a chemical reaction can be achieved by decomposition of just the PCM or by a reaction of the PCM with a substance it is exposed to. Therefore, the first issue to decide for testing is whether the testing is with respect to exposure to a substance, e.g., the atmosphere, or not. However, it is advisable to test the PCM in any case first for decomposition just by itself, in vacuum or inert atmosphere, even if later testing under exposure is desired. Otherwise, if degradation under exposure happens, it is unclear if the reason is a chemical reaction with the exposed substance or if it is simply the decomposition of just the PCM. In any case, verifying if a chemical reaction has taken place by chemical analysis is needed to make sure that no other degradation effect took place. Better is of course even finding out which chemical reaction took place. Care has to be taken when using thermogravimetric analysis, TGA, which determines mass change of a sample exposed to $T(t)$ profiles. First of all, mass change could also be simply due to evaporating sample material into the atmosphere or absorbing, for example, water from the atmosphere, which are both not due to a chemical reaction. Also, a chemical reaction of the sample material itself could happen by thermal decomposition and therefore without overall mass change. The systematic approach used in the previous section, which allows identifying all possible degradation effects, now allows here to identify options for misinterpretation. Besides, it is necessary to also select other testing conditions properly. It is today common knowledge that small heating and cooling rates in calorimeters must be chosen to avoid significant temperature gradients in the sample, which would otherwise lead to inaccurate $h(T)$ results. But that a similar effect is present also in thermogravimetric analysis, and could become significant, has not been tested yet. With respect to accelerated testing the situation is for this degradation effect already well investigated. Common in all cases is that initially the PCM is a stable substance, meaning there is an energetic barrier which does not allow changes at suitable conditions. The existence of an energetic barrier should allow, by variation in conditions, determining its value, and moreover to use it afterwards for accelerated testing. Related publications are, e.g., [11,13,25].

A change in the chemical composition of a PCM from a mixture by unmixing on a larger distance, commonly called phase separation or phase segregation, is a common degradation effect in salt hydrates. Phase separation is commonly discussed using phase diagrams, which show if a PCM changes phase in a congruent, semi-congruent, or incongruent way. Congruent melting occurs if all liquid and solid phases have the same composition; this means, for congruent melting, already the initial step needed for phase separation cannot happen. However, knowledge of what happens in all the other cases, and the consequences for heat storage, is still far from sufficient. Specifically, regarding degradation, the crucial question about phase separation is not its presence but instead if phase separation accumulates, precisely if it accumulates such that the function heat storage, measured by $h(T)$, significantly degrades. Verifying phase separation is simply done again by the determination of the composition, now at different locations in the sample. It is not uncommon that already simple visual inspection is sufficient. Critical, however, are the testing conditions, specifically the exposure to the $T(t)$ profile. Phase separation only occurs if at least one liquid phase is present to allow motion on a large distance, thus that a first test is simply investigating a sample at constant temperature above the liquidus temperature for some time. But phase separation is a complex effect because the underlying mechanism depends on a series of steps: first the formation of phases of different density, then their macroscopic separation, and lack of effective oppos-

ing mechanisms like thermal diffusion or mixing and limiting measures like gelling or thickening. If phase separation accumulates, it thus depends on the balance of separation and opposing mechanisms. For example, already phase diagrams show that in many cases just heating to a temperature somewhat above phase change leads to remixing by diffusion if sufficient time is given for the process to happen. What “sufficient” time means depends on the effectiveness of remixing, by thermal diffusion or by free or forced convection (e.g., stirring), and the distance that phases have separated, limited by the height of the container or encapsulation or further limiting measures like the use of foams, gelling, or thickening. For deeper understanding of how it is affected by conditions, the dynamic processes must be investigated. For $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, Ref. [30] investigated the effect of the cooling rate as well as the effect of the holding temperature in the liquid phase and showed that phase separation can be reversed if appropriate temperature conditions occur during cycling.

4. Discussion

The state of the art today is that PCMs are generally characterized regarding their heat storage capability, sometimes also their thermal conductivity, their viscosity, and not to forget also their compatibility. Long-term performance is tested usually by cycling, meaning by repeated phase change. If possible, cycling is done at application-typical $T(t)$ conditions, but to save time, it is also done at much shorter cycle times. Even accelerated testing by a modification of test conditions, e.g., the temperature a sample is exposed to, has been investigated. However, most of the discussion is on what is tested and how. Ref. [14] concluded that, considering the diversity of the used devices and the wide range of experimental parameters, further work toward a standardization of PCM stability testing is needed.

The analysis thus shows that standardization of testing should not mean to try to define testing in a way that testing is always done with the same methods at the same conditions. This is not applicable as already different applications impose different conditions. But it is also not possible to test everything for reasons of time and experimental effort. Therefore, it is clear that testing should be tailored to the individual case. As the analysis has shown, this is already done in some aspects, however, not systematically. Therefore, here, a “systematic approach to investigate property degradation” with focus to tailor and optimize testing was developed. In Section 3.1.3, the basic functions and related properties that might be subject to testing, e.g., selected with a specific application in mind were first identified. Afterwards, in Section 3.1.4, an approach was given to find the possible degradation effects and underlying mechanisms, to allow tailoring and optimizing test procedures.

As an example, the systematic approach was then applied to the most crucial function and its related property: heat storage enthalpy. With regard to the degradation effects, most of the degradation effects identified by the systematic approach suggested here have already been known; however, surprisingly, also a new one was found: it is the change in the chemical composition of a PCM from a mixture to others just on a small distance. The effect is known in metallurgy; a binary isomorphous system forms different microstructures at equilibrium and at nonequilibrium solidification. With regard to PCM, it has not been investigated yet, and this should be done in the future to complete knowledge on degradation effects. At the moment, this possible degradation effect is not being tested at all due to a lack of awareness. Thus, just testing for degradation effects that are well known from experience is at the risk of missing something crucial. It can, e.g., lead to a misinterpretation of the cause of an observed degradation. With regard to the underlying degradation mechanisms, for most degradation effects the corresponding degradation mechanisms are known, but mostly without details. This lack of deeper understanding of degradation has several serious consequences. For example, for phase separation, the reason, being the first step in the mechanism, is very well known. Opposing measures like thermal diffusion and mixing, and limitation of the distance of phase separation by gelling, thickening, or shallow containers, are also known. What happens in a dynamic situation of repeated phase change has been investigated qualitatively, but is not quantitatively

understood at all. And only if degradation by phase separation accumulates with repeated phase change to a point where the function heat storage has decreased significantly does the degradation become relevant for applications. At the moment, the lack of deeper understanding leads to testing in a very limited way: tests identify if there is phase separation at all and how it affects the enthalpy, all at more or less arbitrary conditions. However, the outcome of testing can strongly depend on the choice of conditions. As discussed before, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ investigations showed an effect of the cooling rate on phase separation, and even more important, showed that if the holding temperature in the liquid phase is chosen appropriately, then phase separation can be reversed. Thus, current testing at more or less arbitrary conditions can lead to a completely wrong impression on the degradation behavior. This is even the case if testing is done at application-typical conditions if extreme conditions occur in an application and cause different degradation behavior. Without a basic knowledge of what goes on, any choice of conditions for testing is at the risk of missing something crucial, but also at the risk of wasting time for testing for something that cannot happen (like phase separation of water). This shows again that standardization of testing should not mean to test always with the same methods at the same conditions, as they are different in different applications. Instead, testing should be tailored to the individual case. For this, the new standardized approach is needed, e.g., using knowledge on the degradation effects and underlying mechanisms to fit test conditions to the application in mind.

The lack of deeper knowledge, however, causes serious problems not only in testing. The lack of deeper understanding how conditions affect the degradation mechanisms usually leads to the attitude to avoid degradation at all costs. Avoiding phase separation in PCM development at all, instead of just limiting it to an acceptable degree, is a significant limitation in the options to choose from and leads to not studying counter measures too. But unless the dynamics of phase separation is better understood, this limitation seems attractive to be on the safe side with regard to degradation. Only for the degradation effect of a change in the chemical composition by a chemical reaction does a deeper knowledge exist, from Chemistry, including the effect of conditions like temperature, pressure, and concentration of substances, and a quantitative understanding in dynamic situations by rate equations. For all other degradation effects, the knowledge is still only very basic, largely insufficient. Last, but not least, an understanding of degradation effects and underlying mechanisms could lead to a reduction in degradation. For example, if a PCM degrades by a chemical reaction with oxygen, it is possible to reduce degradation by adding an antioxidant; e.g., Ref. [11] succeeded in reducing the oxidation of D-Mannitol.

5. Conclusions

The state of the art today is that PCMs are characterized regarding their long-term performance with respect to some commonly used properties, mainly enthalpy change (sometimes also thermal conductivity, viscosity, and compatibility), usually under repeated phase change at application-typical $T(t)$ conditions (sometimes to save time also done at much shorter cycle times). It was shown here that, in contrast to common thinking, future standardization of testing should not mean to simply agree to test always with the same methods at the same conditions because this is not suitable to the large variety of PCMs and applications. Instead, it was shown that testing should be tailored to each individual case following a standardized approach to select what should be tested and at which conditions.

The new “systematic approach to investigate property degradation” developed here identifies first the functions and related properties that might be subject to testing, e.g., with a specific application in mind, and then gives an approach to find the related degradation effects and underlying mechanisms that allow tailoring and optimizing test procedures. This can lead to significant savings in time and testing effort and better results.

As an example, the systematic approach was then applied to the most crucial function and its related property: heat storage and enthalpy. With regard to the degradation effects, by the systematic approach suggested here, a new one was found. The common way of

testing today, to test only for degradation effects that are well known from experience, is thus at the risk of missing something crucial. With regard to the underlying degradation mechanisms, for most degradation effects the corresponding degradation mechanisms are known, but mostly without details. It was shown on the example of phase separation that this lack of deeper understanding of degradation has several serious consequences. Specifically with regard to choosing testing conditions, the example of phase separation showed degradation could even be reversed if the conditions were changed somewhat. Thus, current testing at more or less arbitrary conditions can lead to a completely wrong impression on the degree of degradation.

The lack of deeper knowledge on the degradation effects and the mechanisms behind them, however, causes serious problems not only in testing. The lack of deeper understanding of how conditions affect the degradation mechanisms usually leads to the attitude to avoid degradation at all costs. Avoiding phase separation in PCM development at all, instead of just limiting it to an acceptable degree, is a significant limitation in the material options to choose from. Even more, it also leads to not studying possible counter measures.

With respect to future R&D, the first goal must therefore be to gain deeper knowledge of the degradation effects, mechanisms behind them, and how they are affected by the conditions. Based on that knowledge, the second goal is then to apply the knowledge for individually tailored and optimized testing. The third goal is finally to apply the knowledge for a reduction in property degradation in applications, meaning, e.g., improving PCM by additives such that degradation is reduced.

These goals require a different way of R&D. Up to now, the focus has mainly been on an existing PCM or a potential candidate, which is then tested for degradation of a property value with an established method. However, having the degradation effects and mechanisms behind them as the focus of study, specifically understanding them not only on a qualitative basis but qualitatively to make predictions, PCMs have to be selected that promise learning something about the degradation effects and their underlying mechanisms. While the common way of investigation promises short-term results for a given PCM and its application, this very different way of investigation is required for the long-term development of PCM technology.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: No new data were created or analyzed in this study. Data sharing is not applicable to this article.

Conflicts of Interest: The author declares no conflict of interest.

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