Phase Change Monitoring for Energy Content Determination in Gelled Latent Heat Storage Using Electromechanical Impedance Spectra

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ABSTRACT

To mitigate climate change, a more sustainable and efficient use of resources is crucial. As approximately 50 % of energy consumption is attributable to thermal applications, insulation materials and thermal management offer great potential for savings. Latent heat storage materials (phase change materials - PCM) are suitable for storing and releasing large amounts of thermal energy, e.g. in industrial waste heat recovery, off-peak power generation, solar power plants, food industry, spacecrafts and medicine. In 2022, we were able to show that the use of sorbitol-based organogelators together with polyolefins allows the production of form-stable gels from organic PCMs. Unlike traditional PCMs, these gels do not flow in the molten state and show very low leakage and high energy storage capacity. This work presents a novel approach to determine the stored energy content in these form-stable PCMs using the electro-mechanical impedance (EMI) spectrum, for which a patent was recently filed. Piezoelectric elements, embedded within form-stabilized, organic PCMs, can detect and quantify the degree of phase transition from solid to liquid (and vice versa). Additionally, this method can potentially monitor the condition of implemented PCM systems, as the detection of potential leakage and degrading of materials is a common application for EMI and ultrasonic waves.

INTRODUCTION

Not only sustainable energy production, but also responsible use are among the most important challenges of our time. In Germany alone, 8,667 PJ of energy were consumed in 2021, 58.9 % of which in thermal field of application, with room heating (28 %) and process heat (22.6 %) having the greatest impact [1]. There is enormous potential for savings here, which can be achieved by optimising existing systems or developing new innovative solutions. For example, latent heat storage systems that use phase change materials (PCM) already have a wide range of applications. These materials have a high enthalpy of fusion, which makes them excellent energy storages. They are well estab-

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lished in solar energy storage [2], heat recovery in industrial processes [3], temperature control in electrical applications [4] and heat storage in buildings [5]. The energy storage function is particularly interesting for future applications. With the increasing use of renewable energies, which are subject to natural fluctuations in production, it is necessary to store energy for days or weeks at a time [6]. This is exactly what latent heat storage systems can provide, while being robust, durable and long lasting [7].

The materials used as PCM have in common that they have a high phase change enthalpy. Both, organic materials such as waxes [8], fatty acids [9] and polyethyleneglycol [10] and inorganic materials such as salts and salt hydrates [11], are used. The choice of materials depends on the application and the required melting temperature. As the phase change can cause problems in some cases due to leakage, PCMs are often encapsulated or immobilised [12, 13]. In 2022, we showed that the use of sorbitol-based organogelators together with polyolefins allows the production of form-stable gels from organic PCMs. Unlike traditional PCMs, these gels are incapable of flowing in the molten state and show very low leakage and high energy storage capa-city [14].

Although PCMs are very promising, they are currently only used sporadically. An important reason for this is the inadequate determination of the state of charge. Depending on the material/material mixture used, most PCMs have a melting point or a narrow melting range. As most of the energy is stored in the phase change, a temperature measurement (which remains constant during the phase change) is not suitable for determining the energy.

This work presents a novel approach, setting the basis for determining the stored energy content in these form-stable PCMs using the electro-mechanical impedance (EMI) spectrum, for which a patent was recently filed. The patent also includes the usage of ultrasonic waves, which is not part of this publication. The aim is to use the EMI measurements to quantify the degree of phase transition from solid to liquid (and vice versa). Additionally, EMI and ultrasonic waves can potentially monitor the condition of implemented PCM systems, as the detection of potential leakage and degrading of materials is a common application for both.

MATERIAL AND METHODS

Synthesis of form-stable PCM-composites

Paraffin wax mixture from Rubitherm (RT55) were used as PCMs. The number indicates the average melting range. The gelator used was 1,2,3-trideoxy-4,6:5,7-bis-O-[(4-propylphenyl)methy-lene]-nonitol (TBPMN) from Milliken (trade name: Millad NX8000). The polymer used were Stamylan P, isotactic polypropylene (iPP), Mw $\sim$300 kg/mol.

To produce a form-stable PCM composite, 96 w% RT55 (PCM component) and 2 w% iPP (polyolefin component) are heated under stirring to 170 °C in the absence of air until a homogeneous solution is produced. The temperature required depends on the melting temperature of the polyolefin used (140 °C is sufficient for polyethylene). As the gelator degrades slowly under prolonged thermal stress, it should only be added once the polymer has completely dissolved. 2 w% TBPMN (gelator component) are added to the homogeneous solution and the temperature is increased to 220 °C. When a clear bluish solution has formed, the magnetic stirrer is removed and the heating is stopped.

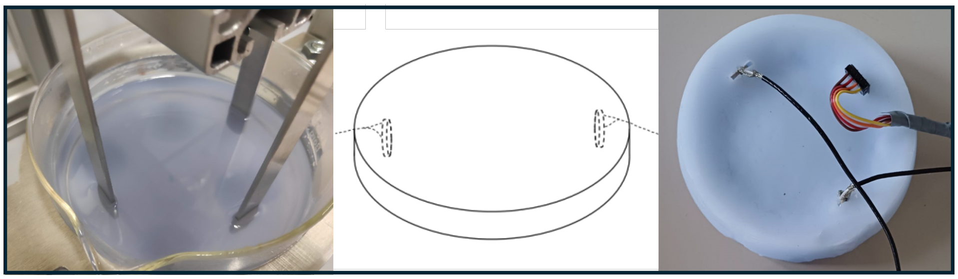

Figure 1: PCM-composite production including the metal spacers (left); schematic drawing of PCM sample with embedded piezoelectric elements (centre); PCM sample with piezoelectric elements and temperature sensor (right).

Metal spacers can now be used to create cavities for the later embedding of piezoelectric elements. Gel formation can be observed during cooling. The solution should not be moved until this is complete. Further cooling causes the polymer to crystallise on the gel surface. The sample turns whitish in colour and any bursting elements can be carefully removed. The resulting gel body can now be removed from its mould (before the PCM crystallises). To do this, it is necessary to use a thin spatula to detach the edges from the container and slightly deform the body to bring air under its base. Figure 1 shows a schematic representation of the structure. Leven et al. described deeper insights into the structure formation in 2021 [15].

Experimental Setup

The electromechanical impedance (EMI) is a complex-valued, frequency-dependant measure of resistance to mechanical and electric vibration. Using piezoelectric elements, mechanical and electrical impedance are combined. The EMI of the piezoelectric element depends on inherent mechanical and electrical properties, such as density, Young's modulus, dielectric constant and geometry, as well as boundary conditions, such as the amount of surface in contact with surrounding material, the inherent properties of the surrounding material and temperature [16]. Therefore, the EMI can be used to determine properties of the environment of a piezoelectric element, which has been used in different SHM applications (e.g. [17, 18]).

For optimal measurements, the piezoelectric elements need to be in full contact with the PCM. As their Curie temperature is close to that of the gel formation for most piezoelectric materials, they have to be inserted at a later stage. The cavities created by the spacer are used for this purpose, see 1. Alternatively, the molten PCM can also be cut with a scalpel and the piezoelectric element inserted with tweezers. As the gel bodies with liquid PCM are slightly flexible, this minimally invasive procedure is not a problem for the integrity of the sample.

In total, five samples have been produced for measurements. Their dimension are 10.5 cm diameter, 2.5 to 3 cm height and 170 to 200 g of material. Two different piezoelectric elements with dimensions 10 mm diameter with 2 mm height (type A) and 20 mm diameter with 2 mm height (type B) were used. While type A is embedded using the prepared vertical cavities, type B is embedded via a horizontal cut in the gel body. Details regarding the specific number of temperature cycles and piezoelectric elements used can be found in table I. However, not all measurements are considered, as a few

TABLE I: Sample test details.

sample ID	piezoelectric elements used	number of temperature cycles
1	A, A	2, 4
2	A	2
3	A, A, B	2, 4, 2
4	A	2
5	B	2

piezoelectric elements broke quickly during tests lacking electrical closed circuit.

The prepared samples are placed in an oven (Premiere DHG-9030) and preheated to 45 °C before temperature cycles for phase change start. To sufficiently quickly melt the samples, the temperature was set to 65 °C (10 °C above the designed melting point) and kept at that level until a high-resolution temperature sensor (ADT 7422), which was also placed inside the sample, did not show a significant change of temperature for at least 30 minutes. Subsequently, the temperature was lowered to 45 °C again for solidification. One full cycle took at least 5 hours. During this process, the piezoelectric elements (material: PIC255 by PI Ceramic) were excited using the Bode100 Vector Network Analyzer in an automated manner using Python. While early measurements were done in 5-minute intervals this was later lowered to be done as fast as possible, which is just under 2 minutes with the chosen settings (6401 spectral points on a linear frequency sweep from 50 to 600 kHz). With the choice of RT55, which is designed with a wide range of phase change, and the high-resolution temperature sensor present, it was possible to a) determine the range of phase change from the temperature data, and b) use the temperature data as a rough reference for this approach. Only data that was determined to be measured during phase change is considered in the results.

RESULTS

Synthesising the gel composites is quick and easy. As the materials used do not conduct electricity, the piezoelectric elements do not need to be encapsulated separately, but can be inserted directly into the sample. The slightly flexible gel matrix is not being damaged when working carefully and ensures good contact between the measuring elements and the sample. If the sample does become damaged, it can either be remelted and recycled or repaired with an additional amount of hot PCM-gelator-polymer solution. The gel bodies ensure that the measuring elements cannot move and are therefore stationary. This is necessary for the subsequent evaluation of the measurement data.

From the EMI measurements, the authors collected 18 features in total from the resistance and the susceptance spectrum. Mainly the stochastic moments from 2nd to 4th order, spectral centroid, spread and entropy as well as some peak related features. Figure 2 shows the resistance and susceptance spectra from two phase changes, melting and solidification, of sample 5 from 80 to 130 kHz including the first eigenfrequency. The temperature range for melting is 52.7 to 58.4 °C and the solidification range is 56.4 to 50.2 °C, showing a difference of roughly 2 °C between the two processes. The data shows a gradual change of amplitude and frequency of the eigenfrequencies. In between eigenfrequencies, there are virtually no changes to observe.

Resulting features from EMI spectra show some desired behaviour, especially skew-

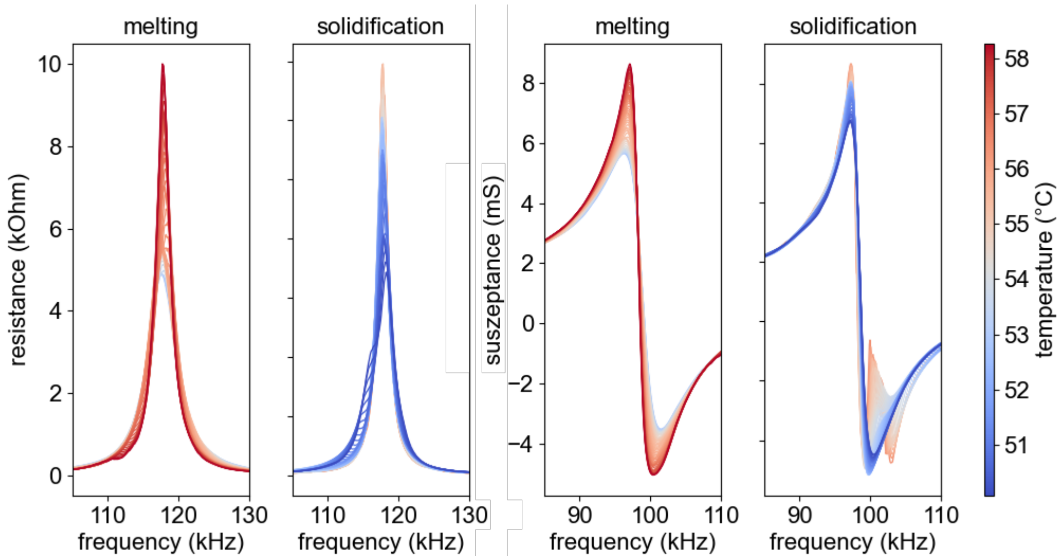

Figure 2: Changes of the EMI spectrum due to melting and solidification of sample 5, measured with a type B piezoelectric element.

ness, centroid (susceptance) and entropy (resistance) are close to monotonic functions especially in the region of phase change. Results in general are repeatable, although differences from the same sample and piezoelectric element are clearly visible. Melting and solidification of the same sample and piezoelectric element do not necessarily show the exact same behaviour in their respective phase change temperature range for all features. Additionally, feature shifts occur in both temperature and feature value, as well as stretching of features (fig. 3). While repeatability and consistency of measurements of the same sample and piezoelectric element are high, the sample to sample variability is more significant. Results from piezo type A, not shown here, embedded into the samples using the premade cavities, show similar behaviour, albeit with increased variance and less consistency.

DISCUSSION

The novel approach to determine the degree of phase change in a PCM in this work shows promising results. Measurements during temperature cycles from a single sample are not only highly consistent, but several features extracted from the spectra exhibit monotonic behaviour during the phase change, which is ideal. Further, some features show remarkably similar trends, but are shifted along the temperature axis. This indicates that even for PCMs specifically designed to be monitored by temperature sensors, such sensors may still yield ambiguous or unreliable readings. In contrast, the EMI-based method is able to distinguish these cases clearly and, once implemented at a higher TRL, is expected to offer significantly more robust and reliable monitoring.

While there are many positive observations, the results in general also indicated that reliable data acquisition among different samples is still difficult. Despite having multiple virtually identical samples, variability can be significant. This is one reason why the implementation method from piezoelectric elements type A was changed for the type B elements. As the prepared cavities provide means of easy insertion of piezoelectric elements and minimise the invasive procedure, they were probably oversized. The size,

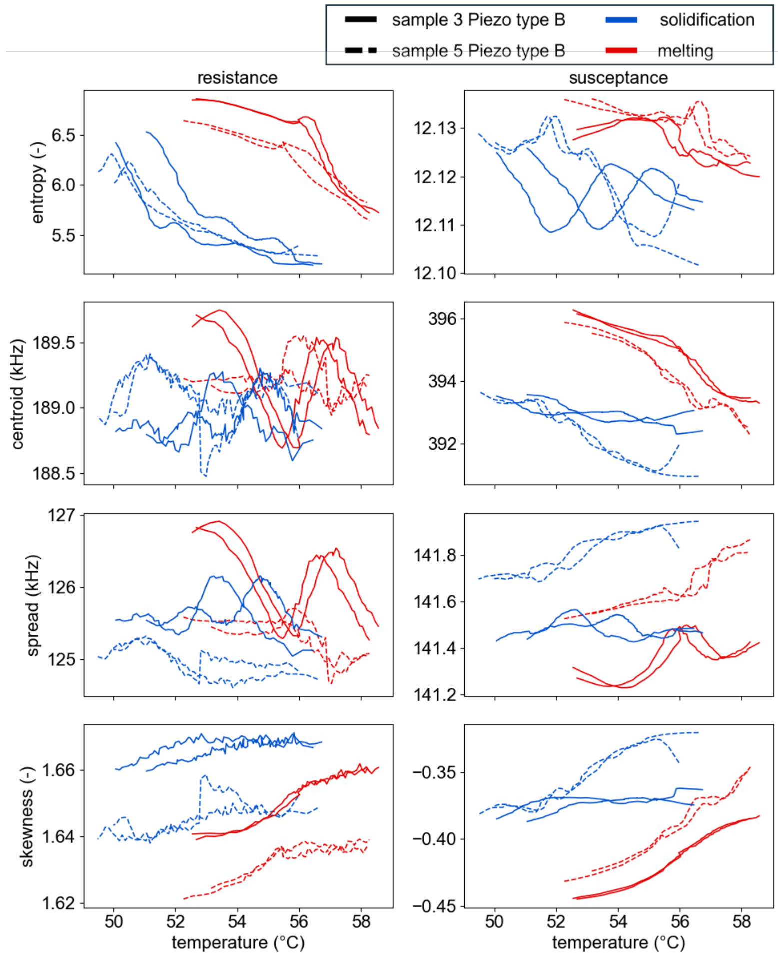

Figure 3: Results of selected features from two different samples for the resistance (left) and susceptance spectrum (right). Each sample was exposed to two temperature cycles.

shape and position of the piezoelectric elements are equally important. Moreover, for type A elements their position inside the PCM, vertical - along the depth profile for almost the entire sample, was likely suboptimal. Later tests using multiple temperature sensors confirmed that the samples were thin enough to avoid edge effects at the element positions, therefore keeping them comparable. Size and shape of the piezoelectric elements not only determine their modal parameters, which are the most important parts of the EMI spectrum, they also define the spatial region of the sample which can be observed and should be carefully chosen.

Notable differences were observed between melting and solidification. These are likely due to two main effects: First, melting and solidification do not follow identical paths, as both processes begin at the sample boundaries and progress inward. As such, the measurement results are expected to reflect this asymmetry to some extent. Additionally, the piezoelectric elements themselves have inherent properties changing with temperature, such as eigenfrequency, capacity and charge constant, which influence the results. Another effect which may influence the measurements is the pyroelectricity, which also polarises the crystal and changes direction with the temperature gradient, therefore amplifying the effect during temperature cycles.

CONCLUSION

The work presented here introduced a novel approach for determining the degree of phase change in a given material using the electromechanical impedance (EMI) spectrum. The authors decided for the paraffin wax mixture RT55, with a wide temperature range of approx. 6 °C for the phase change, allowing temperature measurements to act as reference measurement. With this material, a form-stable PCM composite with 2 w% polyolefin and gelator was produced. The form stability allowed for easy insertion of the piezoelectric elements used to perform measurements of the EMI spectrum. The prepared samples of PCM, equipped with piezoelectric elements and a temperature sensor, were then exposed to temperature cycles from 45 °C to 65 °C and back, covering the phase change range and adjacent temperature in both directions.

From the EMI spectra, 18 features in total were extracted, showing varying results. Most features showed consistent behaviour during temperature cycles and some even have monotonic characteristics. Further, features can show similar trends, but shifted along the temperature axis, suggesting that even in a somewhat ideal application for a temperature sensor, ambiguity can still be present and that this approach is able to distinguish these cases. The difference in results between melting and solidification is probably caused by the temperature-dependent properties of the piezoelectric elements, as well as a possible influence of the pyroelectric effect. However, some of these results only hold if applied to observations of a single sample. When comparing to other identical samples, larger differences arise, making comparability difficult in some cases.

The focus in future work should lie on achieving high consistency of manufacturing and measurements among different samples. The potential use of nonlinear combination of features, using e.g., self-organizing maps, support vector machines, etc. was only tested on a small subset showing promising results. It will potentially help to overcome the sample to sample variability and should be tested. Additionally, this will allow future work to expand its scope to influences beyond the current such as different material contents, different temperature gradients, different shapes and sizes of samples and the possibility to monitor long time performance.

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