



## **Application of polyamide 6 as a phase change material: Preliminary studies**

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### **Abstract**

Phase-change materials (PCMs) have been the subject of numerous studies for many years thanks to their ability to accumulate heat from phase transitions. This group of materials is different to conventional groups, such as metals, polymers or ceramics. A PCM can be any material with specific parameters, such as the temperature of the phase transition suitable for the application, high enthalpy of the transition, easy product availability or a relatively low price. Applications for this type of material are numerous – from construction, where they are used to collect heat for cooling and heating buildings, through water heating, collecting heat from solar panels, creating smart textiles for athletes and people working in changing weather conditions, to planned applications in food packaging to keep food at the right temperature for longer. Corrosion issues with common PCM salts used in a medium temperature range (150–250°C) induced the development of chemically nonaggressive materials. Due to its high availability, satisfactory melting point for use in heat accumulators and relatively low price, polyamide 6 was used in a series of tests. Polymers are not a popular material for PCM due to their low melting enthalpy and fast degradation. Static temperature exposure tests were run and the first cooling curves were examined to determine whether polyamide 6 is a suitable PCM for this application. The results obtained so far are optimistic, but further tests will be required to determine the performance of the material during repeated charging and discharging cycles of the heat accumulator (heating and cooling of the polymer).

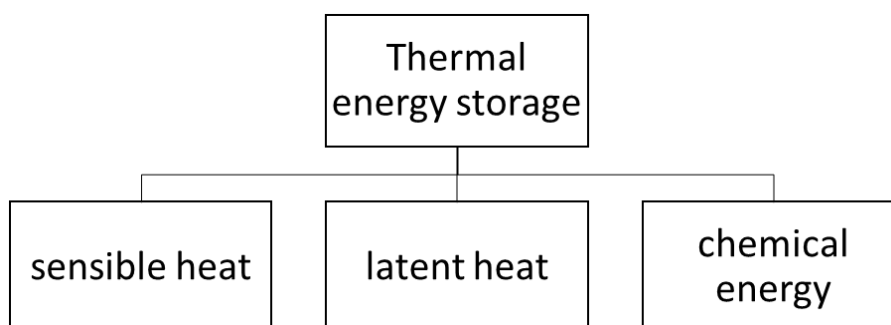
Keywords: PCM, polymers, polyamide 6, heat storage

## 1. Introduction

Due to the numerous problems associated with the pollution and destruction of the environment caused by the exploitation of oil, coal and wood to generate heat, renewable energy sources are becoming increasingly popular among researchers, investors and entrepreneurs. The possible accumulation of energy in various forms has therefore become the subject of numerous studies and publications. However, obtaining energy from mechanical sources, such as wind or water flow, is not a convenient and universal way to be used in all applications. Therefore, a great deal of attention is paid to the accumulation of thermal energy, among other things [1].

The storage of heat energy is a particularly important aspect due to the worldwide demand for hot water, which has so far been heated by conventional energy sources (such as wood, coal and natural gas), and cooling – removing heat from the air to reduce the temperature in rooms for various purposes. The stored heat can be used for reheating the room, for example at night, when the temperature decreases.

Thermal energy is stored in several different ways, which is directly related to the types of thermal energy. Figure 1 shows the basic division of types of thermal energy storage.



**Fig. 1.** Classification of thermal energy storage materials [2], [3]

We can divide thermal energy storage materials according to the origin of the stored heat. In the case of thermal storage directly related to the material's heat, we can distinguish between sensible heat accumulators (stored by increasing the temperature of the material – for example, sand, water or rock [4]) or latent heat accumulators (the stored heat allows for a change in the state of aggregation – when returning to the first state of aggregation the heat is released to the environment) [5], [6].

Materials for storing latent heat are called phase change materials (PCMs). They are known for their relatively high enthalpy values for a phase transition, such as melting, and thus for the large amount of thermal energy required to move from one physical state to another [7].

## 2. Phase change materials

Materials that store heat through a phase transition, PCMs, are characterized by a narrow temperature range in which the phase transition can occur. During this phase transition, the temperature of the material does not rise and all heat supplied is used to break the bonds and stimulate the particles to move. The higher the energy required to complete the phase transition (i.e., the higher the heat value of the material), the more efficient a PCM can be obtained from it.

### 2.1. Key requirements for PCMs

A material considered as a PCM should be able to meet a series of requirements for different properties. These include primarily thermal properties, of which the melting point will play a key role, depending on the intended use. A large heat transfer surface is essential; this can be modified during the design of the tank or battery. Moreover, a large thermal capacity and a high heat of fusion are also important.

When it comes to physical properties, the criteria are related to the transition the PCM will undergo. For all types of transition, it is crucial to limit changes to the volume during the phase transition as much as possible. In the case of a solid–liquid transition, the melting process is expected to occur evenly throughout the whole system volume, and the resulting liquid should have a relatively high density. In the case of gaseous transitions, it is necessary to maintain a low pressure of the vapours generated during the transition.

There are also numerous chemical requirements, the most important of which are long-term thermal stability, which will allow multiple loading and unloading of the stock, as well as a low toxicity, non-flammability and corrosion resistance. These features will allow for safe use at home and will guarantee the lowest possible impact on the users' health.

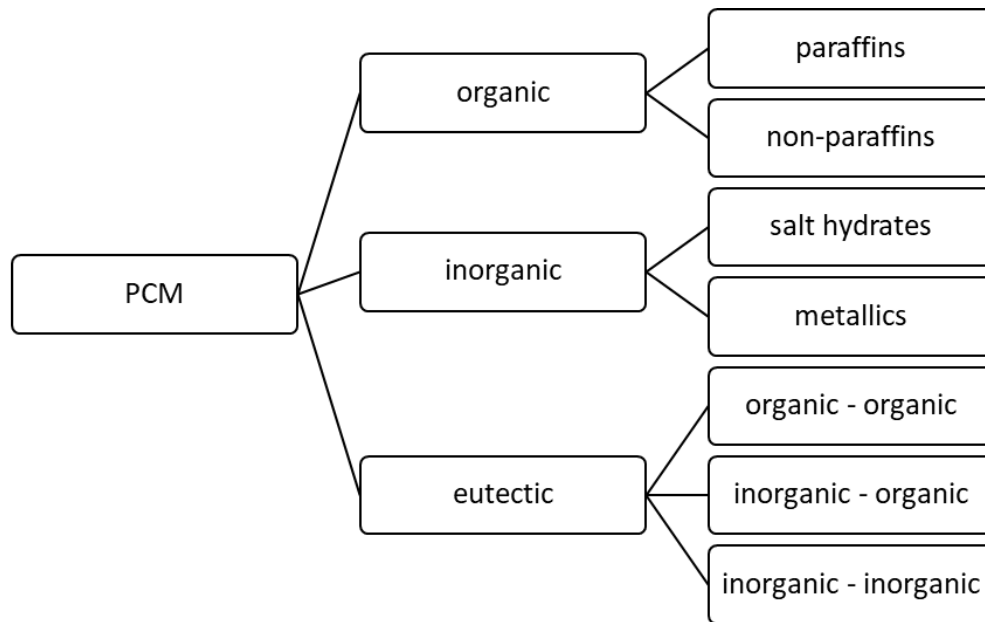
Finally, economic requirements should be fulfilled. The material should be easy to access and, consequently, cheap and in large quantities. In this case, the use of recycled materials can be considered if all the above expectations are fulfilled [1], [4]–[6].

### 2.2. Classification of PCMs

The general classification of PCMs is based on their chemical nature. Therefore, they are usually distinguished between

- organic PCMs,
- inorganic PCMs, and
- eutectic PCMs [8].

The classification is presented in Figure 2.



**Fig. 2.** Classification of PCMs based on the type of material [1]

Among organic PCMs, paraffin and non-paraffin compounds are most often defined. Non-paraffins include polymers, which are the subject of the research described in the following sections.

Paraffins, waxes, are usually mixtures of alkane chains characterized by high latent heat which increases with chain length. They are valued for their low cost, non-toxic, non-corrosive nature and stability over a relatively large temperature range. Since paraffin starts to degrade above 500°C, it is used mainly for low-temperature applications [1], [4], [6].

Non-paraffins are mainly fatty acids (formic acid, hydrocinnamic acid, hypophosphoric acid, etc.), alcohols, esters or glycols. Their advantages include high melting temperatures, non-flammability and a low flashpoint, but, on the other hand, they are often marked by low thermal conductivity and instability at high temperatures. The low thermal conductivity can be improved by placing metal inserts or fillers inside the PCM deposit in order to distribute the heat throughout the deposit volume. Metal inserts, metal foams, metal or metal oxide particles and graphite in the form of particles and expanded particles are suggested for that application [9]. Non-paraffins are often toxic substances.

With inorganic PCMs, salt hydrates take the most important position. Eutectic or non-eutectic mixes of salt hydrate compounds are usually used to gain a high heat of fusion and the expected melting temperature, but the demand for congruent melting must be considered. Popular salt hydrates include  $\text{NaNO}_3$ ,  $\text{NaNO}_2$ ,  $\text{KNO}_3$  and LiK compounds with LiF or magnesium salts [6], [10].

Metallics are mostly eutectic alloys containing Bi, Pb, Ga and In [6].

## 2.3. Applications of PCMs

PCMs have been recognised as a useful and interesting solution in many areas of life and industry. The most developed areas of application are sustainable construction, energy management and renewable energy sources. There are many publications on the use of PCMs in solar energy. They have been described in detail by [11]. The authors highlighted the fact that PCMs allow high thermal storage density and can work in various temperature ranges. Applications have been described in which PCMs are used to collect heat from a liquid heated by solar or photovoltaic panels, which can then be used in everyday applications such as heating floors or water in radiators and heating water for the kitchen and bathroom. For that application, organic (paraffin waxes) and inorganic (hydrated salts) PCMs are suggested. Other interesting applications have been described by [12], where encapsulated PCMs are incorporated in the pavements to reduce extreme temperatures on the pavement surface, thus reducing the degree of freezing on cold days and overheating on warm days. A similar study, this time for use in asphalt, was presented by Wei et al. Microencapsulated PCMs were placed in an asphalt binder mix. This allowed the temperature changes in the bitumen to be slowed down by almost 10°C [13]. The application of PCMs in the automotive industry has also been studied [14]. PCMs have been suggested as an energy source to power batteries, but so far only theoretical studies and a literature review have been made.

Encapsulation of PCMs has recently also been used to create thermo-regulated smart textiles. Hydrocarbons and inorganic salts are suggested for this application. A PCM is placed on the textile by adding capsules to the polymer solution from which fibres are created, or by laminating and coating ready textiles. The PCM is usually placed in a hard polymeric shell [15]. There are also numerous publications connected to the application of PCMs in the food industry as an innovative material for temperature-sensitive food products [16], [17] novel materials with heat management properties have been developed by means of the encapsulation of a phase changing material (PCM).

## 3. Experimental

### 3.1. Materials

So far, the most popular polymer used as a PCM is poly(ethylene glycol). It has been used mainly for encapsulated PCMs [18]. Rarely do thermoplastic polymers appear as PCMs. It was decided to test them due to their satisfactory temperature range, ready availability and relatively small volume change. These polymers have been carefully examined by Weingrill in [7].

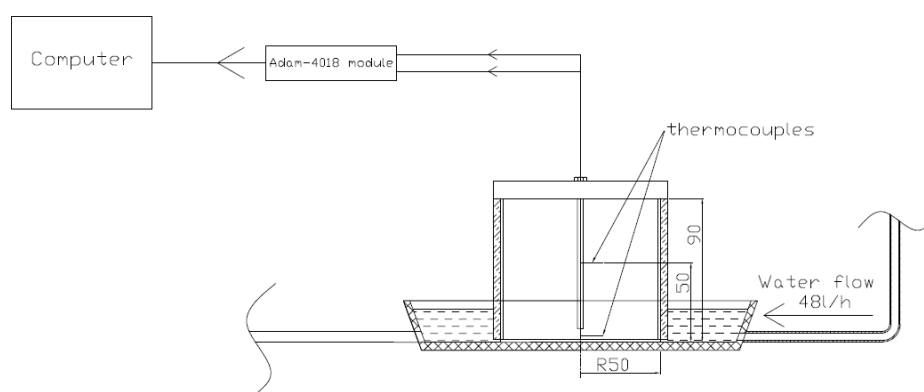
Based on the literature review and preliminary cost determination, polyamide 6 (PA6) was proposed as a potential polymer PCM [7], [19], [20]. Table 1 presents literature data on selected properties of PA6. Tarnamid T-27 NAT, produced by Grupa Azoty, was used in the study.

**Table 1.** Characteristics of polyamide 6

Melting temperature	220°C
Heat of Fusion	50–80 kJ/kg
Specific heat capacity	2700 J/Kkg
Crystallinity	40–50%
Density	1,14 g/cm <sup>3</sup>
Estimated price for 1 kg	9 zł/kg for small amount orders

### 3.2. Testing methods

The testing methods were based on [7]. Tests were run for static temperature exposure in an air atmosphere. Three samples of approximately 100 grams of PA6 granules each, were placed in aluminium crucibles in a convection oven (accuracy: 5°C), which was calibrated before the test. The temperature of the test was set at 250°C, which is approximately 30°C above the melting temperature of the polymer. The exposure times for samples were 120 h, 240 h and 360 h. Before and after the test, the mass of the polymer in the crucibles was determined with a MEDICAT LTD 160 M scale (accuracy: 0.001 g). After the test, the samples were cut in half to investigate the effect that long thermal exposure had on the polymer's physical appearance. The literature review allowed to approximate the composition of the substance created on the surface of the sample. The primary test of thermal cycling was prepared. The cooling curves were measured using an ADAM-4018+ module and the programme Advantech Visidaq. About 400 grams of PA6 were placed in



**Fig. 3.** The test station: the vessel with the melted polymer is in a plastic tray in a water stream. Data from the thermocouples are sent to a computer using an Adam-4018+ module

a steel vessel ( $\varnothing = 100$  mm;  $h = 90$  mm). Two thermocouples (T-203e, K type) were placed inside the vessel – the first at the bottom of the vessel, and the second one centred in the middle of the vessel (about 50 mm from the bottom). A diagram of the test station is presented in Figure 3. The polymer was heated in an air atmosphere to a temperature above the melting point in order to ensure that the melting process was completed. The vessel was placed in a water stream (approx. 800 ml/min; 18°C) in a plastic tray in order to cool down the PCM. The change in temperature of the polymer was measured at different times. The difference quotient was calculated for the results to determine the range of phase transition.

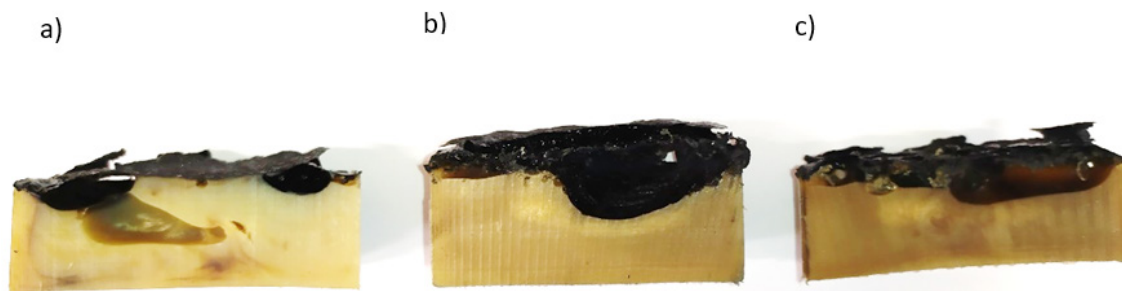
## 4. Results and discussion

### 4.1. Static thermal exposure test

Table 2 presents the change in mass for samples exposed at different times. The test indicates that the longer the samples are exposed to high temperatures, the more material degradation and loss of sample weight can be observed. The results obtained in the experiment were compared with a similar study presented in the literature [7], where after 360 h the mass had decreased by 3.1%. In this study it was 3.68%. In Figure 4 the degradation of the polymer can be seen. In the first sample – exposed for 120 h – brownish spots can be observed. This is connected to the convection of heat and material within the sample. The cavities visible on all the samples are related to the material shrinking during cooling. The change in colour likely appeared due to the formation of chromophore groups after oxidation of methylene groups in the polyamide chain [21]. The dark layer on the top of the samples is a scale, or residues from polymer degradation at temperatures above the melting point. According to the literature, it is mainly  $\epsilon$ -caprolactam, which is a substrate to synthesise PA6 and the products of its degradation. The process should cause a smaller loss of mass if a nitrogen atmosphere is used [22]–[24].

**Table 2.** Change in the mass of the samples after exposure to static thermal load at different times

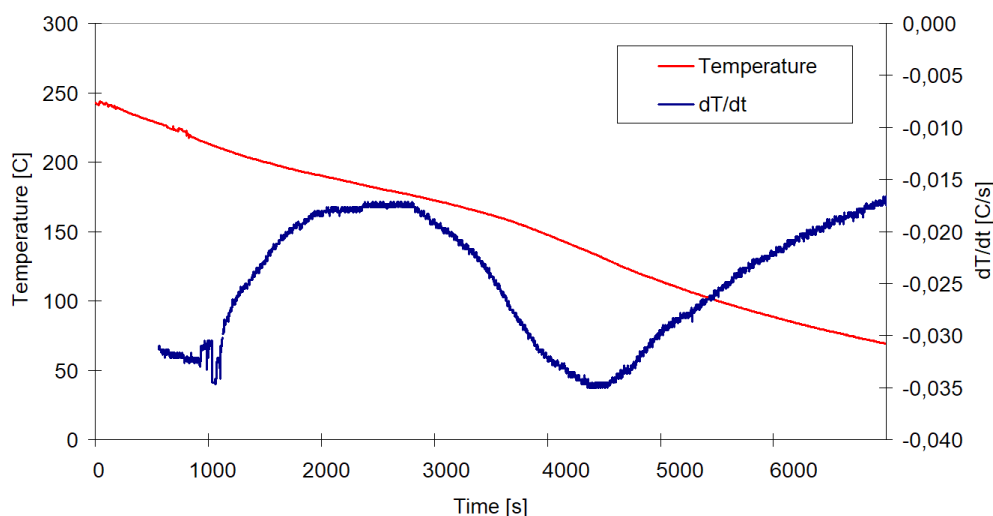
Sample no.	Polymer mass [g]				% of mass lost during the test
	0 h	120 h	240 h	360 h	
1	99,911	98,504	–	–	1,41
2	99,844	–	96,908	–	2,94
3	99,966	–	–	96,291	3,68



**Fig. 4.** Sample of polyamide 6 after static thermal exposure for: a) 120 h, b) 240 h and c) 360 h

## 4.2. Cooling curve analysis

Figure 5 presents an example cooling curve obtained for a sample of PA6. It can be seen that a small flattening appears on the graph at a temperature of about 190°C, which is maintained until the temperature drops to 170°C. A similar situation was presented in the literature [7], [25], [26]. After calculating the first derivative, a stabilisation can be seen in this part of the graph; this entails a transition that will not allow the system temperature to change. This is the recrystallisation of the polymer, which occurs at a temperature slightly lower than the melting point. The temperature of crystallisation may also vary depending on the cooling rate – the higher the cooling rate, the later crystallisation will occur [27]. When the crystallisation is complete, the sample was cooled down to room temperature. After a few thermal cycles (loading and unloading of the PCM), the temperature of crystallisation may change due to the degradation of the material, but it should not be a significant difference. Because PA6 has a slightly different mechanism of degradation in a nitrogen atmosphere, as mentioned before, tests to check the mass difference and degradation process in an inert atmosphere will be taken as the next step of the research.



**Fig. 5.** Differential thermal analysis of a PA6 sample



## 5. Conclusion

PCMs are now frequently tested materials because they have proved to be a relatively cheap and very efficient way to store heat, which often turns out to be a scarce commodity. They have been used in many areas of life and include numerous material groups.

Polymers, especially thermoplastics, are rarely presented as PCMs. Currently, only a few publications have suggested the use of such materials as a PCM. After reviewing the literature on the subject, preliminary studies of polyamide 6 as a PCM were proposed.

Tests of resistance to a static thermal load above the melting point, at 250°C, were performed, which showed slight material degradation in an air atmosphere, which might be reduced by using an inert atmosphere. The first melting cycles were performed, which allowed the range of melting temperatures of the material to be determined. They showed that the crystallisation temperature was about 30°C lower than the melting temperature.

The downsides of polyamide include its organic nature, which limits its lifetime as a heat accumulator. However, due to numerous advantages, such as low cost, small change in volume during melting and crystallisation, ready availability and satisfactory heat capacity, further tests will be carried out to investigate whether changes in conditions, such as the use of an inert atmosphere, a specific charging time or a change in charging speed, will have a positive impact on the use of polyamide 6 as a PCM.

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