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ABSTRACT

The deterioration of perishable food quality due to an interruption in the cold chain might result in food that is unfit for consumption and potentially dangerous. In order to keep the product cold as long as possible, current research is focused on the development of thermally insulated Phase Change Material (PCM)-based packaging capable of keeping products at low temperatures. In this work, an experimental tool has been developed to characterize the thermal behaviour of food while submitted to a temperature rise. The PCM (tetradecane) was inserted in novel biosourced starch films able to trap small droplets of PCM. The effect of the PCM mass fractions in the film on the preservation time of food has been studied.

Keywords : starch films – PCM – food cold storage – thermal insulation – thermal conductivity

1. INTRODUCTION

To preserve the taste and nutritional qualities of food while protecting the health of the consumer, it is necessary to maintain food products under a temperature threshold set by regulation (maximum of 6°C for perishable food). In France, studies shows that 12 % of the transported product presented an average temperature above the recommended value due to cold chain breaks (Loisel et al., 2021).This break can highly impact the product shelf life and quality leading to health problems and food waste with significant economic and environmental impacts. One approach to slow down the heating of products is to use phase change materials (PCM) that are capable of changing their physical state from liquid to solid within a limited range of temperatures allowing the reduction in temperature fluctuations. Many studies have focused on the effectiveness of PCM in extending product shelf life at regulatory temperatures (Leducq, NDoye and Alvarez, 2015; Tas and Unal, 2021) using different concentrations of PCM. However, this solution requires to find the right PCM with its properties that are suitable for food packaging applications and the material that will support this phase change. In addition, PCM must both provide a thermal inertia in the range of temperature conservation and limit the heat transfer flow entering the packaging so the choice of the PCM based on its properties is challenging. If a PCM with a melting temperature below the storage temperature is used, it may freeze the product, and if it is above the storage temperature, it may increase the resistance to temperature changes. Some publications have explored the possibility of using the PCM in bulk form for food applications to provide thermal protection and only few of them explored the possibility to encapsulate the PCM into the films.

Three types of encapsulation exists based on PCM particles size: macro, micro and nanoencapsulated PCM. The micro-encapsulated PCM with the size of 1-1000 um compared to macro-encapsulation, exhibit an homogeneous melting process and can be blended with polymers to form a PCM flexible films (Shi et al., 2021). Moreover, several techniques are used for PCM encapsulation include electrospinning, gelation, emulsion formation, etc. For example, (Hoang et al., 2015) used the technique of electrospinning to encapsulate the PCM in biopolymers and tested different concentrations of polymer and PCM to obtain the efficient amount of encapsulated PCM. (Şahan and Paksoy, 2018) developped a

shapeable polymer composite with PCM capsules by emulsion polymerization. The PCM was encapsulated in two different kinds of shells and then into polymers to form the film shape and effectively, these PCM sheets did not leak during heating and cooling operations so it could be a good idea to apply it as food packaging. (Tas and Unal, 2021) reported the incorporation of PCM into nanocomposite flexible films that can be used for cold storage foods. The PCM were mixed with a stabilizing agent and then was homogenized and 6 melted with the polyethylene (PE) polymer to form the nanocomposite films with 20 wt% PCM and 80 wt% of PE. They elaborated the mechanical properties of the films and evaluated the thermal effect represented by the time-temperature profile of a meat sample coated with 2 different films (standards films and the nanocomposite PCM films). They found that the nanocomposite films has delayed the warming of the meat ball to reach 15 °C by 20 min. (Melone et al., 2012) also microencapsulated the PCM in paperboard matrix with different concentrations but they characterized the films by finding their thermal properties and the heating evaluation. The thermal conductivity of the paper in presence of PCM was lower than that of empty paper. In addition, adding more PCM decreased the films thermal conductivity. Some recent studies have explored the possibility of incorporating PCM in the form of microdroplets in a starch film with a high volume fraction of PCM up to 45 % and identify only the mechanical properties (Jiménez-Saelices et al., 2020). Moreover starch is considered to be one of the most biodegradable polymer for future bioplastics due to its availability and low cost. These first works showed the theoretical interest of such a composite material films, spotting the light on the choice and amount of PCM to be used. Few studies represented the thermos-physical properties of the films e.g the mass heat capacity, the density and the thermal conductivity.

Our work focuses on the use of starch films containing PCM to preserve food at the right conservation temperature. An experimental tool has been designed to study the effect of PCM content in starch film on the food preservation to define an efficient packaging.

2. MATERIAL AND METHOD

The experimental part aims to evaluate the potential use of PCM in films on the shelf life of the product during the heating process. In this context, an experimental setup was chosen, test boxes were designed to represent a simple food container, as well as the selection of PCMs loaded in films. This section describes the device and the experimental protocol.

2.1. Experimental setup

An experimental device (cf. Figure 1) was developed and composed of the main following elements:

• PCM test boxes allowing to integrate starch films.

• A thermal chamber TENNEY brand (model TJR CE-NY-F4T) with an operating temperature between -75 °C and 200 °C, allowing produce temperature cycles: cooling – heating.

• A measurement unit with calibrated thermocouples (uncertainty ± 0.1°C) monitored by a computer

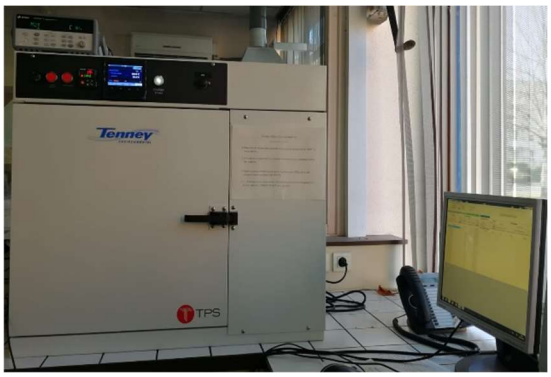


Figure 1: Experimental thermal chamber

2.2. PCM selection

The PCM was tetradecane (TD) a paraffin bought from PCM Products Ltd (PLUSICE A5). It was chosen because its melting temperature (5.83 °C) corresponds to the average storage temperature of food products (0 °C to 8 °C) and its latent heat, L_f = 253 J/g is high. Table 1 presents its thermal properties.

Table 1: Tetradecane properties

	Latent Heat kJ.kg^{-1}	Phase change temperature °C	Density kg.m^{-3}	Heat Capacity J.kg^{-1}.K^{-1}	Conductivity W.m^{-1}.K^{-1}
Solid	253	5.83	880	1680	0.2
Liquid			760	2180	0.15

2.3. Test boxes

Test boxes made from polyethylene terephthalate glycol (PETG) of cubic shape, 5 cm on each side, have been manufactured by 3D printing. The box (Figure 2 and Figure 3) allows the integration of the films in the 4 side walls. The idea was to find an approach to test the films on the product noticing that the films were not flexible, so a solution was found in reference (East, Smale and Kang, 2009) to fix the films around the box with covers. A test product was placed in the centre of the box. It is a parallelepiped of methylcellulose with dimensions ($3cm \times 3cm \times 2cm$); this material was chosen because it has thermal properties close to those of food. A support with 4 elastics bands and 2 insulated lids (top and bottom) were used to maintain the films around the box and to limit heat transfer through the top and bottom walls of the box (Figure 3.

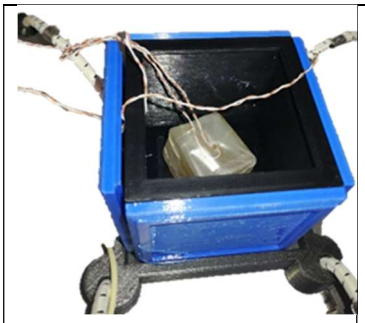
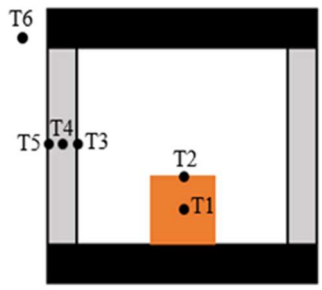


Figure 2: Test Box

Figure 3: Inside the box

Six T type thermocouples were used to follow the temperature evolution of different parts of the box: methylcellulose (center T1, top surface T2), wall (inner T3, outer T5), on the film surface (T4) and the air in the thermal chamber (T6). The positions of these thermocouples are shown in Figure *4*.



T1	Product center
T2	Product top surface
T3	Inner wall
T4	PCM (films or bulk)
T5	Outer wall
T6	Thermal chamber

Figure 4: Thermocouple position

2.4. Starch films

Films of starch alone or incorporated with tetradecane were produced at UR1268 Biopolymers Interactions Assemblies - BIA. In order to be introduced in the test box, they were cut into squares (46 mm x 46 mm x 2 mm). The fabrication procedure of these films was described in (Jiménez-Saelices et al., 2020). They produced the films with an aqueous suspension of rod-like chitin nanocrystals (ChiNCs) mixed with paraffin oil, and form an oil-in-water Pickering emulsion with a droplet diameter of 3 µm. These emulsions mixed with a 5 wt% starch solution formed homogeneous composite films by solvent casting. Four types of films were tested in this study (Figure *5*): starch alone (0 % TD), starch with tetradecane at 5 % and 15% mass fraction (5 %TD and 15 %TD).

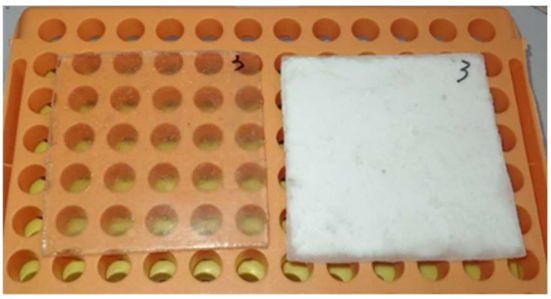


Figure 5 Starch films with and without PCM

Table 2 shows the properties of the materials used. The temperature T_f and the heat of fusion L_f were obtained by DSC (Differential Scanning Calorimetry) measurements, the thermal conductivity of the films by the C-THERM Trident instrument measurements. The density and heat capacity of the films were calculated.

Table 2: Material properties

	L_f	T_f	ρ	C_p	λ
	$kJ.kg^{-1}$	$°C$	$kg.m^{-3}$	$J.kg^{-1}.°C^{-1}$	$W.m^{-1}.K^{-1}$
Starch film	-	-	1085	1345	0.036
5 % TD	8.676	5.58	1062 (liq)	1709 (liq)	0.22 (liq)
			1072 (sol)	1683 (sol)	0.24 (sol)
15 % TD	32.46	6.56	1018 (liq)	1803 (liq)	0.2 (liq)
			1046 (sol)	1726 (sol)	0.22 (sol)
Wall (PETG)	-	-	1270	1170	0.34

2.5. Experimental protocol

The starch films and methylcellulose were first weighed and then added to the box (Figure 2. The thermocouples were installed in their positions and then the box was closed with the holder (Figure 3) and placed in the thermal chamber at 20 $°C$. When the core temperature of the product stabilized at the selected temperature, a cooling cycle was started by setting the chamber temperature at -0.6 $°C$ to ensure that the PCM was completely solidified and the product temperature was at 0 $°C$. In the range of 4-6 $°C$, we can see an inflection of the slope related to the phase transition

from liquid to solid state of PCM (T4) due to the tetradecane in the films. Once the system is stable at 0 °C, a heating process will begin by setting the chamber temperature to 20 °C (Figure 1).

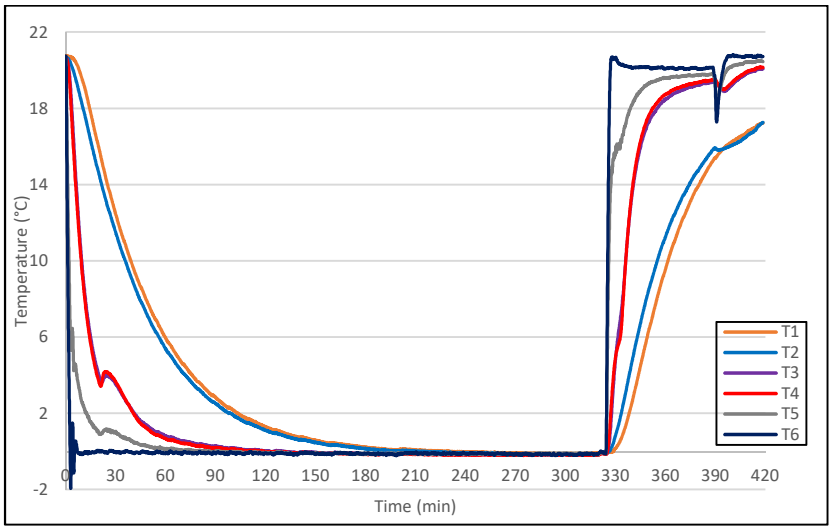


Figure 6: Exemple of cooling and heating process with 15 %TD films.

3. RESULTS AND DISCUSSION

In this section, the effect of starch films loaded with different mass percentages of tetradecane on the product will be discussed.

3.1. Bio-based starch films with PCM

The first experiments are carried out on a reference case, i.e., the box without films, in order to show the impact of the presence of the starch film with or without PCM.

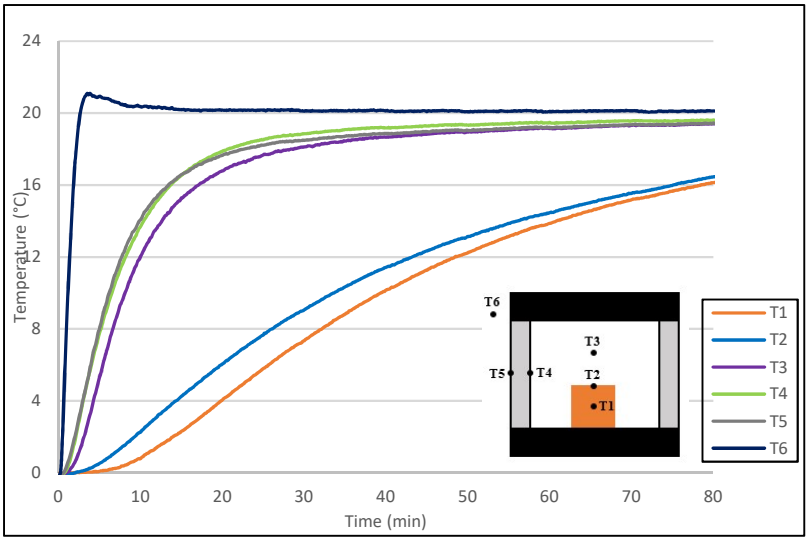


Figure 7: Heating process of an empty box

Figure *7* shows the temperature evolution in the box without films. By setting the temperature at 20 °C, the chamber heats up in 3 min only. The inner and outer walls behave in the same way, which is logical since there is only a small air gap between the walls. As the inner surface of the box is large, the indoor air takes time to warm up, which influences the heating of the methylcellulose. At the product level, we noticed a difference in heating time at the beginning

between the upper part and the centre due to heat transfer, then the temperature homogenizes in the methylcellulose after 80 min. The addition of a starch film without PCM is compared with the behaviour of the empty box in Figure *8*.

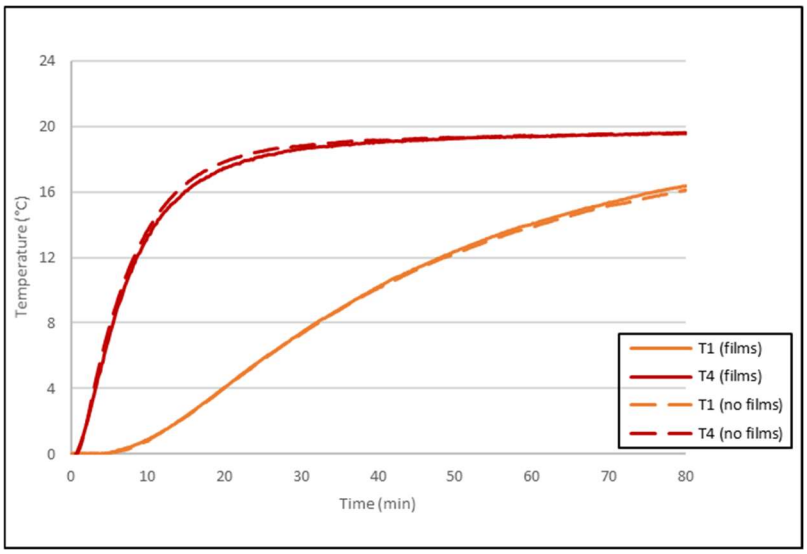


Figure 8: Thermal behaviour of a box with and without starch film

Figure *8* illustrates the temperature evolution at the films (T4) and on the methylcellulose centre (T1). To compare the two cases, we supposed that T4 (no films) corresponds to the inner wall temperature in the box without films. There is no significant difference on temperature evolution in the presence of the films. This can be explained by the fact that starch films have a very low thermal conductivity (measured 0.036 W $m^{-1}K^{-1}$), close to that of air (reference 0.025 W $m^{-1}K^{-1}$). It should be noted that during the phase change the film thickness remains constant, as no swelling or shrinking occurs on the film. After the study of virgin starch films, we examine the evolution of the box temperature with films loaded with 15 % mass percentage of tetradecane (15 %TD).

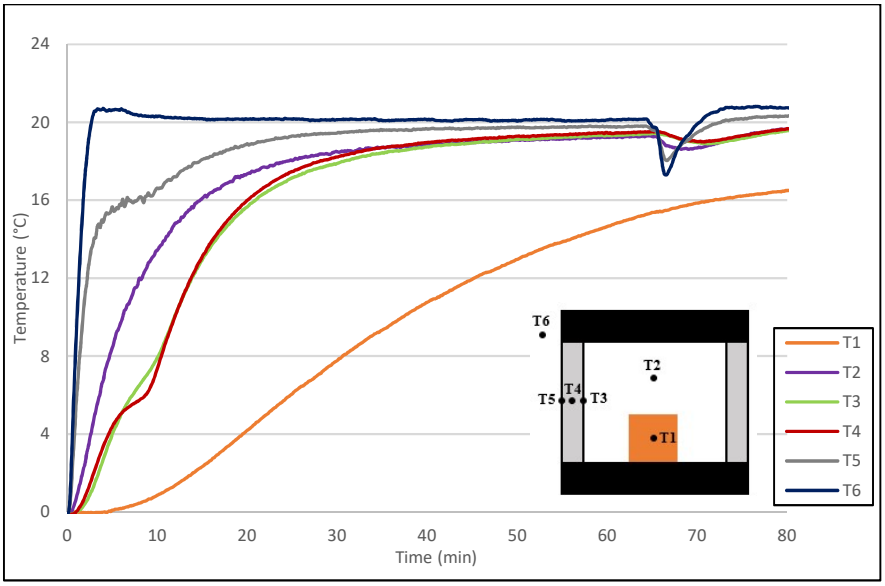


Figure 9: Evolution of temperature in the box loaded with 15% TD

Figure 9 represents the temperature evolution in the box with 15 %TD loaded films. During the heating process, the thermal behaviour is modified by the effect of the latent heat of PCM. In addition, between 60 min and 70 min, a sudden deactivation of the thermal chamber (T6) takes place, which also changed the thermal behaviour in the box. The phase change in the films (T4) is detected near 5.5°C (slope inflexion), which corresponds to the melting temperature of

tetradecane. This transition from the solid to the liquid phase of tetradecane influenced the behaviour of the inner wall but not the air inside the box.

To see the effect of adding PCM (tetradecane) to the films on methylcellulose, we compare the three types of films containing different mass percentages of tetradecane (0 %, 5 % and 15 % w/w).

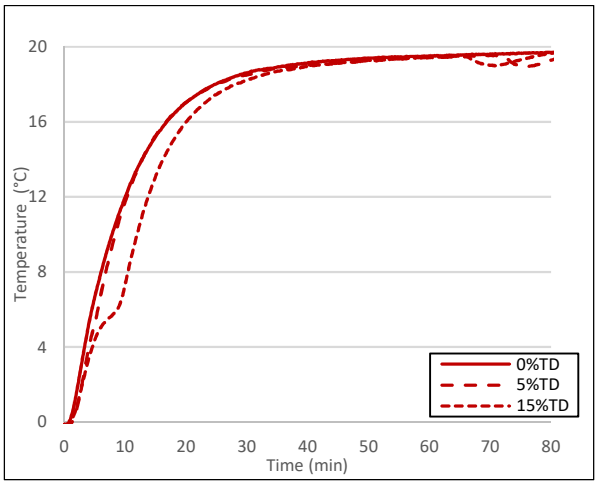


Figure 10 Temperature evolution of films loaded with different mass % of tetradecane (T4).

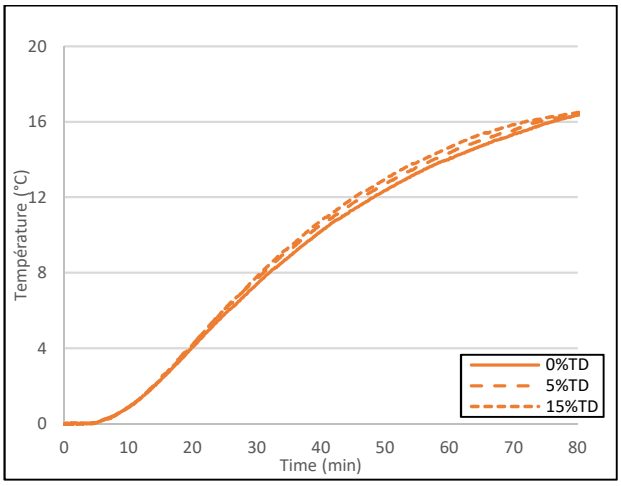


Figure 11 Temperature evolution of methylcellulose (T1) with films loaded with different mass % of tetradecane.

Figure 10 shows the temperature evolution of the films filled with 0 %, 5 % and 15 % w/w tetradecane. The phase change plateau with 15 % is very noticable at a melting temperature of 5.5 °C whereas it is negligible for the 5 %TD films. Therefore, the length of the phase change plateau depends on the amount of tetradecane. Adding 5 % of tetradecane in the film produces a slight difference in the temperature evolution which can be explained by the increase of the thermal resistance of the wall.

The effect of the amount of tetradecane on the methylcellulose is represented in Figure 11. At the beginning, the behaviour was the same with the three types of films but after 20 min, a deviation of the curves is noticed. From an initial perspective, we expected to see the product resist to temperature increase after the addition of tetradecane, but the results present the opposite, i.e., the performance of the methylcellulose is better with the virgin starch films. As shown in Table 2, the addition of PCM seems to minimize the insulating effect on the product. In fact, the thermal conductivities in liquid state found for 5 %TD and 15 %TD films are 0.15 $W.m^{-1}.K^{-1}$, that is significantly higher than that of virgin starch films 0.05 $W.m^{-1}.K^{-1}$. As soon as the tetradecane melts, the insulting effect decreases (the liquid conductivity is higher than solid conductivity) and the product temperature raises.

In order to maintain the flavour and nutritional value of the food while preserving the health of the consumers, the food must be kept below the legal threshold (8 °C for perishable foods). In the next step, Table 3 shows a comparison of the conservation time of the product with different films for three different temperature ranges (0 °C to 4 °C, 0 °C to 6 °C and 0 °C to 8 °C).

From Table 3 it is noticed that methylcellulose performs better with starch films (0 %TD) even if the time difference is negligible (0.5 min for 0 °C to 4 °C and 0 °C to 6 °C and 1 min for 0 °C to 8 °C. Indeed, the starch film is a good insulation material, equivalent of that of air, so adding the paraffin decreases the performance of the insulation.

Table 3. Comparison of methylcellulose heating time in the presence of tetradecane loaded films.

Films	Δt from $0°C$ to $4°C$	Δt from $0°C$ to $6°C$	Δt from $0°C$ to $8°C$
	min	min	min
0 %TD	20	25.5	32
5 %TD	19.5	25	31
15 %TD	19.5	25	30.6

These results are in disagreement with the current papers. (Melone et al., 2012) studied the encapsulation of PCM in a paper matrix with two different concentrations (25 and 50 % w/w) for the design of a cold storage package and measured the thermal properties. They obtained as thermal conductivity for the paper matrix made of cellulose 0.1085 $W.m^{-1}.K^{-1}$. After adding PCM with melting temperature between 0 °C and 10 °C, they found (0.0913 and 0.0819) $W.m^{-1}.K^{-1}$ for 25 %w/w PCM and 50 %w/w PCM respectively. In terms of heat transfer for cooling applications, the lower the thermal conductivity value, the higher the heat resistance and the longer the shelf life of the product.

In our experiments, the results are obtained with a very low amount of paraffin and the contribution of the phase change energy is not sufficient to modify the thermal behaviour. It can be expected that with a higher percentage of paraffin in the film the food preservation would be better. The phase change temperature of the paraffin is also an important parameter, and it could be expected that lower the phase change temperature c would provide a longer preservation time.

4. CONCLUSION

This study has focused on new food packaging containing phase change material to increase the product shelf live. A new starch film has been developed for this purpose, it can contain small droplets of PCM. The experiments have been carried out in test boxes that can include the starch films with two different amount of PCM 5 % and 15 %. The thermal behaviour of a product placed in the centre of the box has been studied for different cases. The experiments surprisingly show the best behaviour with the starch films without PCM. This is due to the low conductivity of the starch film compared to that of the paraffin, especially in the liquid case. The effect of the PCM is noticeable as the food preservation time his lower with the highest amount of PCM. Thermal properties of the PCM are essential to obtain higher performance of the system. Indeed, phase change temperature, latent heat and conductivity are major properties that affects the thermal behaviour. Also, the amount of PCM that can be included in the starch film should be increased. Modelling of the heat transfers will be developed in further work to optimise the thermal behaviour of the product.

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