Polypropylene characterization by Differential Scanning Calorimetry (DSC)

Angeline Kpeusseu Kouambla Yeo, Bati Ernest Boya Bi, Paul Magloire Ekoun Koffi, and Prosper Gbaha

Laboratoire des Procédés Industriels, de Synthèse, de l'Environnement et des Energies Nouvelles (LAPISEN), UMRI 18, Institut National Polytechnique Félix Houphouët Boigny (INPHB), B.P. 581, Yamoussoukro, Côte d'Ivoire

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ABSTRACT: *Objectives:* The objective of this work is to study the thermal behavior of polypropylene (PP) as phase change material (PCM) with the aim of its use to store energy necessary for cooking in the event of energy deficit for the solar cooker.
Method: We used the differential scanning calorimetry (DSC) method for different speeds, both heating and cooling. We have identified the phase change temperatures of the different samples as well as the evolution of the crystallinity rate of each sample.
Findings: The first heating measurement of the sample is carried out to remove its thermal history. The additional heating measurements gave us information on the behavior of the material (Peak of melting: 167.24°C; Heat of fusion: 86.50 J/g). The cooling measurements gave us access to information such as the differentiation of materials with different histories. The crystallization peak of the recycled material is wider and lower than that of the new material. The temperature peaks of all the curves are around 120°C.
Novelty: The use of the MCP allows us to make a solar cooker autonomous, because the energy stored at the level of the MCP, can ensure the cooking of food during the day in the absence of sunlight and also during the night.

KEYWORDS: Polypropylene; Crystallization; Heater; Cooling; PCM; Store.

1 INTRODUCTION

This work is part of the cooking of food by solar energy. Indeed, the depletion of energy resources has motivated the search for new energy sources. Thus, several researchers have embarked on conquest of new energy sources such as renewable energies (solar, wind, biomass, etc.) in order to satisfy cooking [1]. The culmination of their labors were the direct and indirect cookers. However, they were faced with a problem, which was the autonomy of indirect cookers. Indeed, the intermittent nature of solar source is highlighted in periods of overcast skies or in the evening at sunset.

The problem posed is: How to ensure the autonomy of indirect solar cookers?

To try to solve it, we propose to use polypropylene as a phase change material (PCM), to store the energy necessary for cooking in the event of an energy deficit.

In this case, the characterization of recycled polypropylene with a view to its use as PCM in our solar cooking device is necessary, since it can allow us to know the capacity of this material to store energy and release it when appropriate.

Solar, as the most abundant source of energy among all renewable energies, is generally transformed in toother more exploitable forms of energy (kinetic, thermal or electrical energy) for its use.

The collection of solar energy can be done by two distinct techniques: flat collectors and solar concentrators [2, 3].

The thermodynamic conversion of solar energy most often uses parabolic tank solar concentrators (PTSC), in particular in the industrial and domestic field which require an operating temperature range between 80°C and 160°C [4 – 6]. Although this energy passes through the PTSCs, the challenge is to store it, since the PTSCs lose their capacity under an overcast sky or in the evening when there is no sun.

For a good estimate of the efficiency of our system, it is desirable to determine the polypropylene's heat capacity after several heating-cooling cycles. This parameter is essential for the calculation of thermodynamic quantities of the material.

Its possible determination thanks to the calorimeter can be done at constant pressure Cp or at constant volume Cv. A calorimeter is a container in which thermal phenomena occur subject to measurements; There are several models including differential scanning calorimetry (DSC). It is the latter we used in our study. It made it possible to obtain cooling curves for eleven (11) samples, 10 of which were recycled. Which curves were then interpreted and revealed the exothermic behavior of the samples. The results of the curves being practically similar, we have chosen to present four (4) curves on the eleven (11) samples.

2 METHODOLOGY

2.1 EXPERIMENTAL PROCEDURE

The simplest definition of heat capacity is as follows [7, 8]: Quantity of energy required to increase one gram of matter (or one mole) by one degree Celsius. But this other definition does not take into account certain measurement conditions such as: temperature, pressure, volume etc. Depending strongly on temperature, heat capacity is expressed in form of a function that can be determined from internal energy U for Cv and enthalpy H for Cp. Thus, their mass expressions are as follows:

$$C_v = \frac{1}{m}\left(\frac{\partial U}{\partial T}\right)_v \tag{1}$$

$$C_p = \frac{1}{m}\left(\frac{\partial H}{\partial T}\right)_p \tag{2}$$

Its unit in International System (SI) is J. K^{-1}.kg^{-1} but in a practical way the measurements are expressed in J. K^{-1}g^{-1}.

Given difficulties associated with their determination, heat capacities are quantities resulting from a derivation. Different methods of measuring this parameter exist. But the nature of products, the range of measurement temperature envisaged as well as precision sought are all elements will influence choice of method. We will present here only method of differential scanning calorimetry (DSC). It is a method based on temperature variation. This method is suitable for heat capacity measurements but for limited temperature ranges [9 – 12]. Despite delicacy of its implementation of methods using this technique (DSC), the accuracy of results is possible thanks to measurements in a relatively short time interval.

The ISO 11357 standard illustrates the principle of DSC in figure 1.

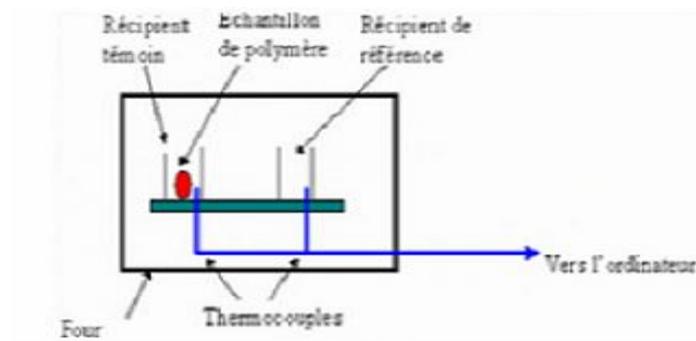DSCs exist in two forms:

- With heat flow,
- With power compensation.

Fig 1 : Operating principle of a dsc machine.

2.2 METHODS

In this work, we used DSC method for different heating and cooling rates.

We have identified the phase change temperatures of different samples as well as evolution of crystallinity rate of each sample.

Inside the same oven, DSC has 2 cells. One contains the sample and other the reference. We performed analysis of 11 standard polypropylene (PP) samples in Table 1.

The recording of DSC curves was done on a METTLER TOLEDO DSC1 machine in figure 2 inside which there are HSS8 sensors and a liquid nitrogen cooling accessory.

Fig 2 : Dsc 1 mettler toledo dsc 1 Machine

The samples, which had not undergone any prior treatment and weighed between 5 and 15 mg, were introduced into standard aluminum crucibles (figure (3, 4)) of 40 µL capacity with a pinhole.

The weighings were possible thanks to a Shimadzu-AUW220D balance (figure (3, 4)).

Fig 3, 4 : Crucible – Weighing scale

The samples underwent several cycles of heating from -100° C to 250° C with one minute of holding at isothermal temperature at 250° C followed by cooling to 25° C at a rate of 10° C/min.

Heat exchanges can be modeled by the following relationships:

$$
\begin{cases}
\phi_e = \dfrac{T_{fe} - T_e}{R_e} \\[2mm]
\phi_r = \dfrac{T_{fr} - T_r}{R_r} \quad \text{(J/s or Watt)} \\[2mm]
\Delta\phi = \phi_e - \phi_r
\end{cases}
\tag{3}
$$

Where R_e is sample thermal resistance and R_r is reference thermal resistance with respect to oven.

T_e, T_{fe}, T_r, T_{fr} respective temperatures of sample, oven wall on sample side, reference, oven wall on reference side. The recording of $\Delta\phi$ will be done as a function of time at a constant or variable temperature.

$\beta = \partial T / \partial t$, the representation of heat flux $\Delta\phi$ (denoted ϕ for simplicity) will be expressed as a function of temperature or time. The measurements are made under an atmosphere of neutral nitrogen gas.

2.3 EXPERIMENTAL WORK

2.3.1 POLYPROPYLENE'S CHARACTERISTIC

It's part of family of thermoplastics, hot-formable without chemical modification and easily recyclable. Characterized by its great inertia to chemical attacks, its high impact resistance and its melting temperature is between 160°C and 170°C. Polypropylene has many advantages: it is cheap, food-grade (odorless and non-toxic) resistant to fatigue.

2.3.2 OPERATING MODE

The following steps were performed:

1. Open liquid nitrogen valves (4 in total);
2. Turn on machine (DSC);
3. Prepare sample;
4. Close DSC oven;
5. Use of METTLER TOLEDO software for data processing (entering protocol, name and mass of sample).

All this allows us to draw representatives curves of our experience.

DSC measurement curves show the peak (figure 4a and 4b) whose air corresponds to enthalpy involved in process. These curves highlight typical thermal effects when material is heated. These include exothermic and endothermic peaks namely glass transition temperature (Tg), peak due to cold crystallization, enthalpy of fusion and finally decomposition. The crystallinity value for melting (Xm) and cooling (Xc) was determined using following equations [13 – 17]:

$$
X_m = \frac{\Delta H_m}{f.\Delta H^\circ} \times 100
\tag{4}
$$

$$
X_c = \frac{\Delta H_c}{f.\Delta H^\circ} \times 100
\tag{5}
$$

Analysis of curves takes into account thermal history of material. Obtaining final shape of curve is done by removing isotherms. In ourwork, the amount of material to be used is much greater. It is therefore not obvious that all the material changes state in a homogeneous way. Size and distribution of crystallites is all more important since it gives us information on endothermic or exothermic nature of material.

3 RESULTS AND DISCUSSIONS

Differential scanning calorimetry (DSC) study is carried out to understand the phase inversion behavior (crystallization and melting) of a material when subjected to heat [18].

Here the samples were heated and cooled at a constant rate (10 K/min) and the different states of the samples were measured as a function of temperature.

The black curve (figure 4a) highlights first heating run. It illustrates the typical effect observed on heating. The first event is the glass transition temperature, which can be seen as a step-in curve. This is followed by exothermic cold crystallization peak and endothermic melting peak. If the samples were heated at higher temperature, it will start to decompose. The temperatures

at which these effects are likely takes place are characteristic for each particular material [13, 14]. The DSC curves can therefore be used as a finger prints in quality control [13 – 17]. Generally, the first heating measurement is performed to remove the thermal history of the sample (Polymer) which may be due to the processing conditions induced during sample preparation [13 – 15]. In generalities often very useful to measure the cooling curve of the sample and then recording second heating run. These additional measurements provide more information about the behavior of the material [13 – 15]. The second heating curve blue (figure 4a) shows the measurement after removal of thermal history of the sample. The melting peak of new PP is at 167.24 °C with enthalpy value (heat of melting) of 86.50 J/g. The glass transition do not accompany endothermic peak due to enthalpy relaxation. The crystallization peak can be seen in the cooling run shown green line in Fig. 4a. In contrast the new PP was almost completely amorphous because the cooling process during manufacturing was too fast for crystallization to occur [13, 14, 19, 20].

The black curve in figure 4b represents the first heating curve of sample PP_07 (recycled PP). This sample has already undergone 7 heating-cooling cycles. This curve, which is the result of another heating of the sample, has the role of erasing the thermal history of the material [13, 14, 19, 20]. After which, we proceed to the cooling of it. This allows us to obtain the curve in blue (cooling) above the one in black. On this cooling curve (figure 4b), we see that, the exothermic behavior starts from the temperature of 122.67°C and ends at 113.82°C. The peak temperature is reached at 118.36°C. This phenomenon reflects a release of heat which is explained by the presence in the material of a certain rate of crystallites [13, 14, 19, 20]. The amount of energy released during this phase change can be determined through the calculation of the air below each cooling curve, but is also expressed through the software through the value of the integral in millijoule (mJ). Figure 5 illustrates a comparison made between three (3) samples: PP_00 in blue, PP_01 in red and PP_02 in green. The PP_00 sample is new, the PP_01 has undergone a single heating-cooling cycle and finally the PP_02 has undergone 2 heating-cooling cycles. For the same cooling rate of 10 K/min, the exothermic reaction begins at 124.53°C for PP_00, 123.81°C for PP_01 and 122.93°C for PP_02. We notice a delay of this reaction as the number of thermal cycles of the sample increases. Also, at the level of the peaks, we see a drop in their value: 119.87°C for PP_00, 119.46°C for PP_01 and 118.62°C for PP_02. This reflects the drop in the energy released during this exothermic reaction, hence the decrease in the rate of crystallites in the material. The number of thermal cycles undergone by a sample affects the rate of crystallites and therefore impacts its exothermic behavior [13, 14, 19, 20].

The explanation for this phenomenon lies in fact recycled material includes a higher rate of a thermal crystallization seeds. The different peaks in the cooling curves reflect the exothermic behavior of the material during cooling. This is possible thanks to a certain rate of crystallites still present in the material. However, this rate decreases because the polymer chains break as the number of cycles increases. It is therefore possible after a certain number of cycles, the material is no longer capable of releasing heat during cooling. There are grounds to consider renewing the MCP inside our solar cooker.

Table 1 : Thermal history of samples

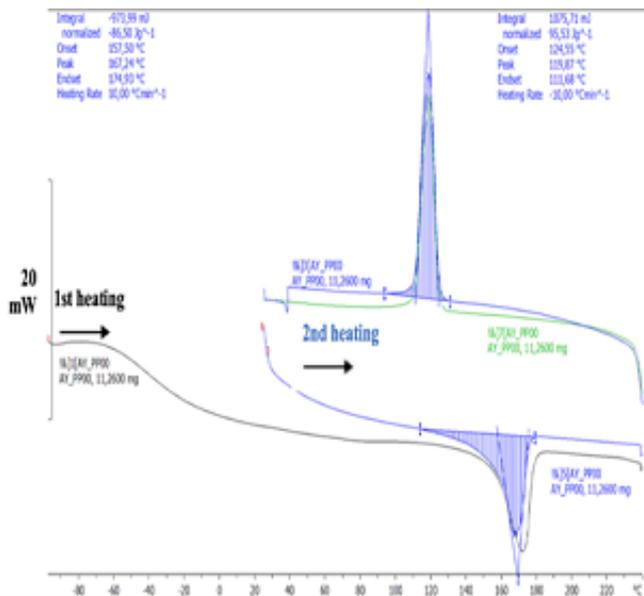| Nombre de cycle → Echantillons ↓	0	1	2	3	4	5	6	7	8	9	10
PP_00 (11,26 mg)	X										
PP_01_New (14,35 mg)		X									
PP_02 (7,06 mg)			X								
PP_03_New (8,04 mg)				X							
PP_04_New (9,13 mg)					X						
PP_05 (7,62 mg)						X					
PP_06 (6,46 mg)							X				
PP_07 (7,94 mg)								X			
PP_08 (7,02 mg)									X		
PP_09 (8,12 mg)										X	
PP_10_New (5,89 mg)											X

Fig 4a : DSC curves of temperature rise and cooling of a new Polypropylene, sample PP_00 ; heating /cooling rate : 10 K/min.
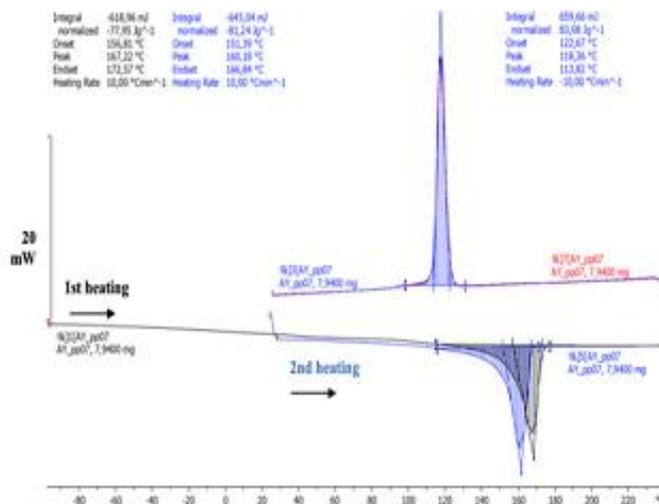

Fig 4b : DSC thermography of PP_07 DSC curves of temperature rise and cooling of a recycled Polypropylene, sample PP_07 ; heating /cooling rate : 10 K/min.
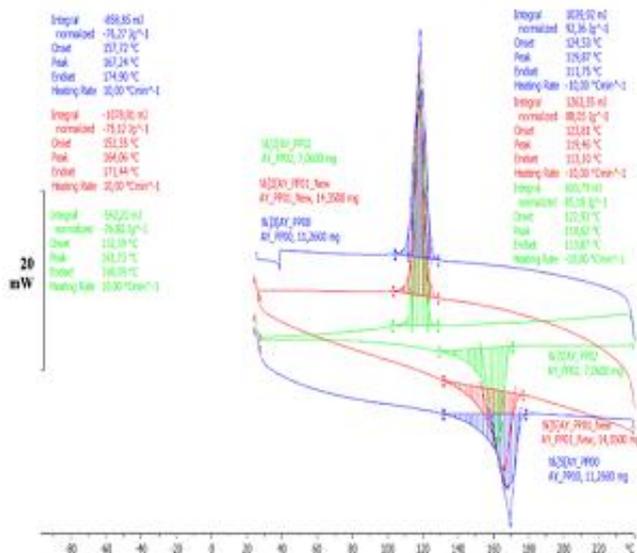

Fig 5 : DSC curves of temperature rise and cooling of different samples (PP_00, PP_01, PP_02) ; heating/cooling rate : 10 K/min.

4   CONCLUSION

At the end of this work, the curves all reveal a temperature peak around 120°C. This temperature is well within the temperature range necessary for cooking. Our PCM therefore has an exothermic behavior which is highlighted through the characterization by differential scanning calorimetric analysis. The element promotes this behavior is its crystallinity. Indeed, the size and distribution of the crystallites are all the more important and give the material an exothermic character. Indeed, the decrease in crystallinity leads to a decrease in the energy released by the recycled polypropylene during cooling. This could allow our appliance to go through several heating-cooling cycles before considering replacing the phase change material inside our cooker.

The perspective we consider through this study is the valorization of the rubber tree by the use of its product which is the rubber.

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