

STSM Scientific Report

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STSM Topic: Comparative analysis of the thermophysical properties of PCM

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Rheological behaviour of Phase Change Materials (PCM). Standardization of the measurement procedure of the viscosity property.

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1. Nomenclature

G' elastic modulus (Pa)	δ phase lag (rad)
G'' viscous modulus (Pa)	η dynamic viscosity (Pas)
G^* complex modulus (Pa)	η^* complex viscosity (Pas)
k thermal conductivity (W/(m ² K))	σ stress (Pa)
r geometry radius (m)	σ^* complex stress (Pa)
Ra Rayleigh number (-)	ω angular frequency (rad/s)
t time (s)	

Subscripts

Greek symbols

γ strain (-)	e effective
$\dot{\gamma}$ shear rate (1/s)	

2. Purpose of the STSM

The work here presented is part of one of the task of the Working Group 1 (New PCM development and characterization) of this COST Action where objectives include to develop standardized methodologies to characterize PCM.

This work is also a part of the work to be accomplished in the Task 42-Annex 24 of the International Energy Agency (IEA). Specifically, this work is included within the development of measuring and testing procedures to characterize new storage materials reliably and reproducibly.

In this case, a standard about the measuring procedure of the viscosity property is going to be aimed.

In the Task 42-Annex 24, there is already much work accomplished about the standardization procedure of the Enthalpy-Temperatures curves with the Differential Scanning Calorimetry. Octadecane has been used, and in the case of the viscosity property, the same paraffin based PCMs has been used. These measurements will be complemented with the measurements of other substances, not pure substances and with substances with the phase change temperature far away from the room temperature.

In general, in the latent thermal energy storage, the PCM is macroencapsulated forming together the heat transfer fluid a storage system. In the present models, the natural convection in the PCM is not usually considered. However in experimental works it has been checked that this term must be considered.

Arkar and Medved [1] already pointed out with their paper the importance in the properties determination. They compared the results of their numerical model with the experimental results. They confirmed their hypothesis on the role so important that the thermal properties of the PCM play, specially in slow running process. Specifically they studied the influence of the Heat capacity-Temperature curve obtained with a DSC for different heating and cooling rate on the results of a TES system with PCM spheres. Regarding natural convection, the first papers that took into account the natural convection are Sparrow et al. [2] and Bathelt et al. [3]. To simulate this heat transfer mechanism, some authors [4-6] consider an effective thermal conductivity:

$$\frac{k_e}{k_l} = c \cdot Ra^n \text{ (eq.1)}$$

Costa et al. [7] studied numerically the thermal behavior of three PCM, a paraffin (octadecane) and two metals, confined in a rectangular domain, where the natural convection in the fluid and the conduction in the solid are both considered. In the case of the octadecane, the authors pointed out a bad fitting with the experimental results in the upper part. The melted liquid on the sides took up the upper part of the geometry, getting faster the melting in this zone. The authors think that the causes of these discrepancies, between theoretical and experimental results, are due to thermal inertias, systems instabilities, thermal losses, lack of reliable information about the physical properties of the materials, 3D behavior, consideration of constant thermophysical properties, density variations, high calculation time and an important change of the viscosity with the temperature. Experimentally, Peck et al. [8] also observed in their T-history installation during the PCM melting that if the tubes were placed in vertical position, a temperature gradient in the longitudinal direction took place due to the natural convection. This caused different melting temperatures in the upper part of the tube.

Since the natural convection depends on the Rayleigh number and therefore on the viscosity, it is necessary to determine the rheological behaviour, and specifically the viscosity property dependent on the temperature, and even in the phase change, in order to incorporate these data in the natural convection simulations.

In the case of PCM slurries, it is necessary to determine the Viscosity-Shear rate-Temperature curves, as PCM slurries are considered a heat transfer and storage fluid. Furthermore, in this case it is important to know the pressure drop that the PCM slurry will cause flowing through tubes and through the typical components of an installation. There are many papers about rheology in emulsions or slurries and some publications about PCM slurries and emulsions where these curves appear. [9-10]. However just one reference has been found in the literature about rheological properties in phase change materials. Their authors analyze the rheological properties of three commercial coconut fats and structure analysis during their solid-liquid and liquid-solid phase change [11].

3. Description of the work carried out during the STSM

3.1 Description of the rheometer

The measurements have been achieved with the control stress rheometer that the research group TAG (Thermische Anlagen und Gebäudetechnik) of Fraunhofer ISE has in its laboratory. It is a rheometer from the Company Thermo Scientific model Haake Mars II. Table I shows the main characteristics of the rheometer and figure 3 shows an image of the equipment.

The measurements presented in this report have been carried out basically with two geometries. These geometries are a titanium plate with a diameter of 60 mm and concentric cylinders, of titanium as well, with an inner diameter of 40 mm. The plate has been used in the case of phase change materials and the concentric cylinders in the case of PCM slurries. In order to control the temperature, a Peltier plate has been used.

The fulfilled tests presented in this report to analyze the rheological behaviour of Phase Change Materials (PCM) are classified in two types of tests: 1) rotational tests and 2) oscillatory tests.

Min. torque rotation CS	μNm	0.05
Min. torque rotation CR	μNm	0.05
Min. torque oscillation CS	μNm	0.05
Min. torque oscillation CD	μNm	0.05
Max. torque	mNm	200
Torque resolution	nNm	0.5
Motor inertia	μNms	10
Angular resolution	nrad	12
Min. angular velocity CS	min^{-1}	1.00E-07
Min. angular velocity CR	min^{-1}	1.00E-04
Max. angular velocity	min^{-1}	1500
Min. oscillation frequency	Hz	1.00E-05
Max. oscillation frequency	Hz	1.00E+02
Normal force resolution	N	0.001
Lift positioning accuracy	μm	0.5
Temperature range	$^{\circ}\text{C}$	-60 to +185



Table I. Specifications of Haake Mars II. **Figure 1.** Image of the rheometer. www.thermoscientific.com

3.2 Theoretical background

The rheometer consists of a 1) drag cup motor that forms the rotating spindle of the rheometer; 2) an air thrust bearing that supports the spindle and 3) an optical encoder that determines the angular position. When using the instrument, the sample is positioned between a lower base (on the Peltier plate in this case) and a removable upper geometry, which attaches to the instrument's rotating spindle. Together, the lower base and the geometry form the measuring system. The lower base forms part of the temperature control system. Moreover, the normal force is measured by a transducer in the lower base that detects the axial force. In this way, this can be used to keep the sample under tension or compression during a measurement. The distance between the Peltier plate and the geometry is called "Gap".

The Peltier plate is the standard temperature control system for the rheometers. It uses the Peltier thermoelectric effect to control the temperature accurately, and enables rapid heating and cooling. The Peltier Plate is basically a disc that has integrated a Pt100 temperature probe, in thermal contact with it and close to the surface. As the metallic surface of the Peltier plate has a very high thermal conductivity the temperature gradients across the surface of the plate is negligible. In this manner, the sample will need an equilibrium time to reach the Peltier plate temperature.

Regarding the tests, the rotational tests entails applying a torque (or stress) and measuring the strain, to obtain in this way, values of viscosity (the rheometer does not measure directly the strain; the strain is obtained from the displacement measured in radians by the sensor and from the gap). The Viscosity-Shear rate curves have been obtained through a shear rate sweep from 0,001 1/s to 1000 1/s. For this purpose, a stress is applied to the sample. The measurement of the viscosity is accomplished when the material has reached the steady state. The stress is increased in logarithm way and the process is repeated, providing the flow viscosity curve.

In the case of the oscillatory tests, the sample is subjected to an oscillating stress of low amplitude and the strain observed by the sample is measured (see figure 1). According to the phase lag between the applied strain ($\gamma = \gamma_0 \cdot \cos(\omega t)$) and the measured stress ($\sigma = \sigma_0 \cdot \cos(\omega t + \delta)$):

- If $\delta=0^\circ \rightarrow$ elastic solid
- If $\delta=90^\circ \rightarrow$ fluid totally viscous
- If $0 < \delta < 90^\circ \rightarrow$ viscoelastic fluid

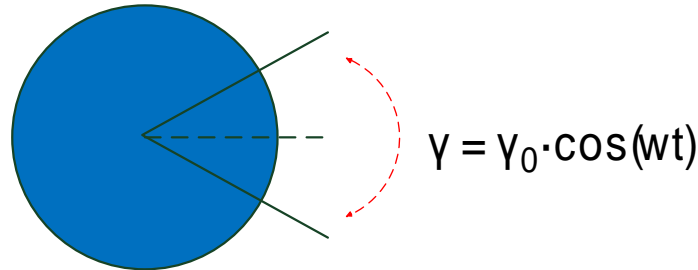


Figure 2. Oscillating strain (geometry, view from above)

In this way, an elastic modulus (G') (that would be the elastic or recoverable part) and a viscous modulus (G'') (that would be the viscous or irreversible part) are obtained.

$$G^* = G' + iG'' \quad (\text{eq. 2})$$

In the left image of figure 2, the curve that it would be obtained in the case of an elastic response is shown, where the oscillating stress would be $\sigma = G \cdot \gamma_0 \cdot \sin(\omega t)$ and the resulting strain $\gamma = \gamma_0 \cdot \sin(\omega t)$. In the right image of figure 2 the curve that it would be obtained in the case of a

viscous response is shown, the oscillating stress would be $\sigma = \eta \cdot \dot{\gamma} = \eta \cdot \omega \cdot \gamma_0 \cdot \cos(\omega t)$ and the strain $\gamma = \gamma_0 \cdot \sin(\omega t - \delta)$.

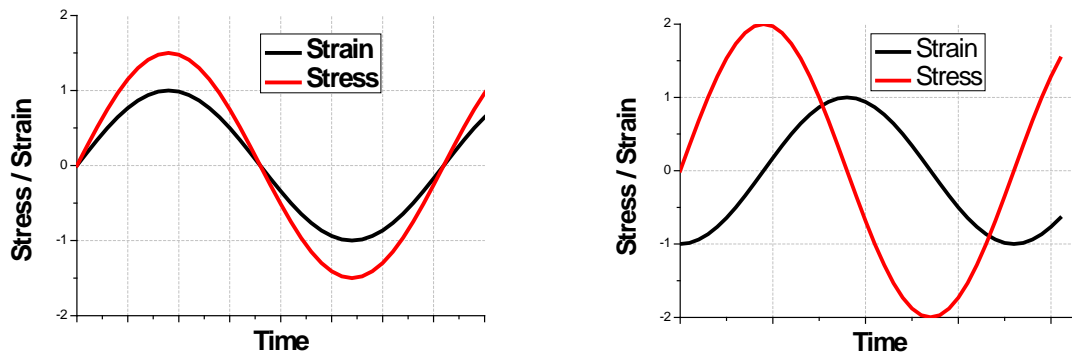


Figure 3. Left image: Elastic behaviour; Right image: Viscous behaviour.

The main fulfilled oscillatory tests have been three: strain or stress sweeps, frequency sweeps and temperature sweeps. In the strain sweeps, a frequency is set for the test, a strain or stress is applied and the response is measured (stress or strain). In the frequency sweeps, the strain or stress is set, a frequency range is swept and the response is measured (stress or strain). In the temperatures sweep, both the frequency and strain (or stress) is set, a temperatures range is swept and the response is measured (stress or strain).

The frequency sweeps here presented cover a frequency range from 0,01 Hz to 100 Hz. These frequency sweeps have been carried out within the viscoelastic region. With this purpose, previously, stress sweeps have been carried out from 0,01 to 100 Pa at a frequency of 1 Hz. The permanence within the viscoelastic region has to be guaranteed above 1 Hz, since at higher frequencies the linear viscoelastic range decreases. It is considered enough at 1 Hz, since above 1 Hz, the measurements present much inertia. The oscillating movement of the axle will undergo a delay introduced by the motor inertia and by the geometry inertia. In the oscillating tests, the inertia is relevant since a phase difference between the applied sinusoidal wave and the responded sinusoidal wave is introduced.

Obviously it is important to know the value of this delay to be eliminated of the responded angle by the sample. The software calculates this value for its correction. In spite of this correction, it is advisable not to take into account the measurements at high frequencies. Besides, in this analysis, measurements at low frequencies are interesting for this work, since the PCM is going to be at rest.

4. Description of the main results obtained

4.1 Analyzed substance: Octadecane (octadecane Parafol 18-97 from the company Sasol)

As it was explained in previous sections, there is a lot of work done with octadecane about the obtaining of Enthalpy-Temperatures curves within the framework of the Task 42-Annex 24 of the IEA. The obtained results for melting curves fit each other quite well. The measurement procedure for the melting curves is trying to be improved. Bigger discrepancies are observed for the solidification curves. Figure 4 shows the melting curves obtained with three DSC from different manufacturers.

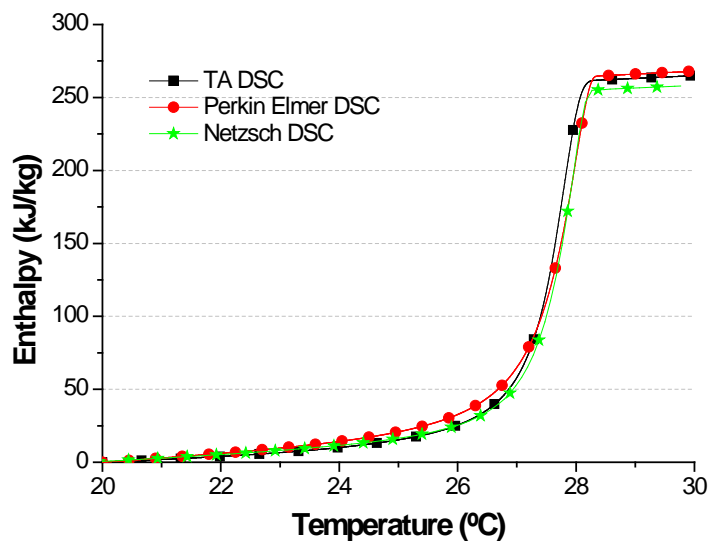


Figure 4. Octadecane Enthalpy-Temperature curve obtained with three DSC from different manufacturers.

4.1.1 First measurements and analysis

When the procedure was written (task to be presented in the last meeting of the Task 42-Annex 24 of the IEA), it was thought that the best way to obtain the viscosity of a phase change material when it is at rest, was obtaining the curve viscosity-shear rate-temperature from rotational experiments. However the first tests showed a considerable variation in the results. When the geometry turned at a specified velocity, this may break the formed crystals, influencing the results in this mode. This is only one of the phenomena that caused wrong measurements in rotational experiments.

In this way, measurements in oscillatory mode have been proposed. First of all, a stress or strain sweep has to be realized, to determine the linear viscoelastic region of the PCM, in this case, the linear viscoelastic region of the octadecane. This region has to be determined for different frequencies and for different temperatures, taking into account that the range of interest is about temperatures within the phase change and very low frequencies (octadecane at rest).

In figure 5, the results derived of these stress sweeps can be observed. It can be observed that at 29°C the G' does not appear, because the PCM is completely melted and its elastic part is so low that the rheometer can not obtain a value. In this case, at this temperature, the PCM has not the linear viscoelastic region because it is a material completely viscous, it has not viscoelastic properties. At 27,6°C (during the phase change), it can be observed that at very low stresses (up to 1 Pa approximately), the measurements have much noise. This noise can be caused for the very low stresses, since the PCM when changing its phase, its viscosity increases abruptly, and very low stresses causes very low strains. These values can be close to the resolution of the displacement sensor of the rheometer. If these values are obviated and just the tendency is observed, it can be

seen that the linear viscoelastic region reaches values up to 100 Pa. The G' modulus does not drop even at this value.

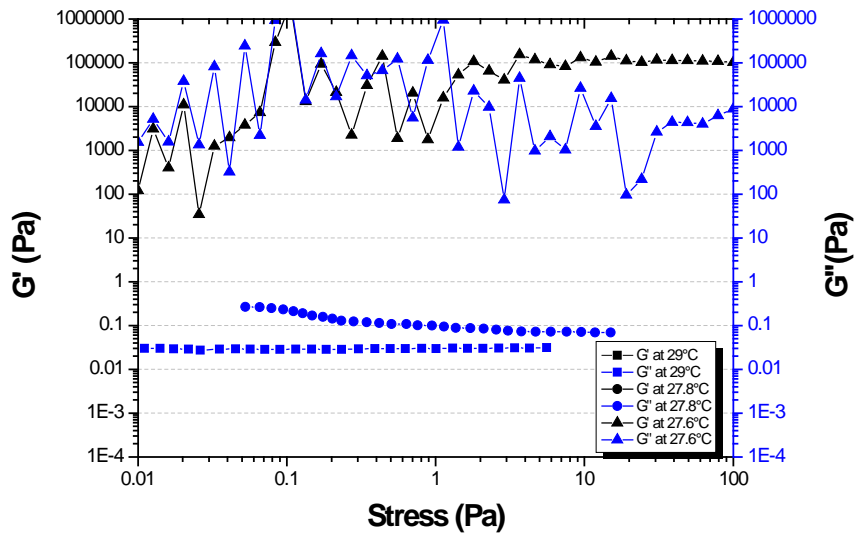


Figure 5. Stress sweep for different temperatures. Frequency=1 Hz

Once the linear viscoelastic region was determined, the procedure “oscillatory temperature steps” has been accomplished for the melting curve. For the preparation of the sample, the sample has been loaded at its liquid phase, and the gap has been fixed so that the sample forms a meniscus. Once the sample is correctly placed between the Peltier plate and the geometry, the value of present normal force has been fixed as reference. In this way when the PCM change its phase, the rheometer will adapt the gap between the Peltier plate and the geometry to have always the same conditions, since with the phase change the sample change its volume, affecting to the force that the geometry makes on the sample. For this reason, the plate geometry has been chosen, to be able to adapt the gap. In the case of the cone geometry the gap is fixed for the geometry.

In figure 6, the results of the procedure “oscillatory temperature steps” compared to results obtained at the University of Zaragoza can be observed. In figure 6, the results of the procedure “oscillatory temperature steps” can be observed, in comparison to the results obtained at the University of Zaragoza. The University of Zaragoza has used a control stress rheometer from TA Instruments, model AR-G2. The procedure was established from temperature steps with a stabilization time of 60s. The temperature steps were 0,1°C. It can be observed in the complex viscosity-temperature curve that about 27,5°C the octadecane changes from solid to liquid.

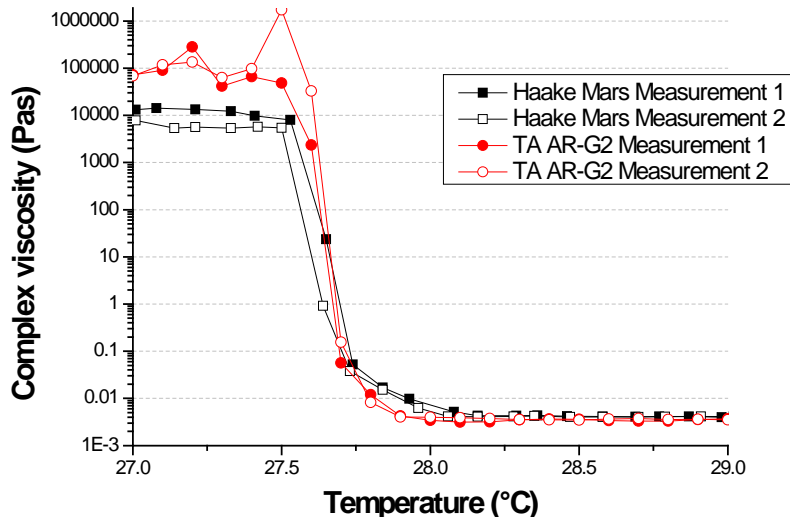


Figure 6. Oscillatory temperature steps. Comparison with the measurements obtained with a rheometer AR-G2 at the University of Zaragoza. Frequency=1 Hz. Stress=10 Pa

The rheometer obtains this complex viscosity of the following manner. The user applies a sinusoidal disturbance and defines the amplitude of the stress (or strain, depending on the mode: controlled stress or controlled strain) and the frequency. In a rheometer, the strain and the stress are calculated as the amplitude of the peaks in the waves of displacement and torque, respectively. The measured change between the input wave and the output wave is the called phase angle. In summary and in our case, a sinusoidal stress is applied to the sample; the response of the material is measured, that is to say, the strain is measured; and the phase angle between the disturbance and the response is measured as well.

The stress in a dynamic experiment is written as a complex stress σ^* , where $|\sigma^*| = \sigma' + i\sigma''$.

The more important viscoelastic parameters are the following:

-The complex module: It measures the resistance to be strained.

$$G^* = \sigma^*/\gamma = G' + iG'' \text{ (eq. 4)}$$

-The elastic module: It measures the elasticity of the material. The capacity of the material to store energy.

$$G' = (\sigma^*/\gamma) \cdot \cos\delta \text{ (eq. 5)}$$

-The viscous module: The capacity of the material to dissipate energy.

$$G'' = (\sigma^*/\gamma) \cdot \sin\delta \text{ (eq. 6)}$$

In this way, for this case, the interest is in the viscous module. The parameter of viscosity will be obtained in the following manner:

$$\eta' = G''/\omega \text{ (eq. 7)}$$

In figure 7, the η' -T curve can be observed, and it can be determined that about 27,5°C the octadecane change its phase from solid to liquid, and values of viscosity are obtained. Maybe the repeatability of the two measurements is not very good. This can be due to the accuracy of the Peltier Plate on the temperature (0,1°C). This value fits with the temperature steps of the procedure. However a step with a higher temperature can not be set, because octadecane is a pure substance and therefore the phase change takes place almost at a precise temperature. The values in solid state must not been taken into account, since the rheometer is not the appropriate equipment to measure the elastic module in solid substances. Probably, the geometry slips with the sample, providing not adequate measurements.

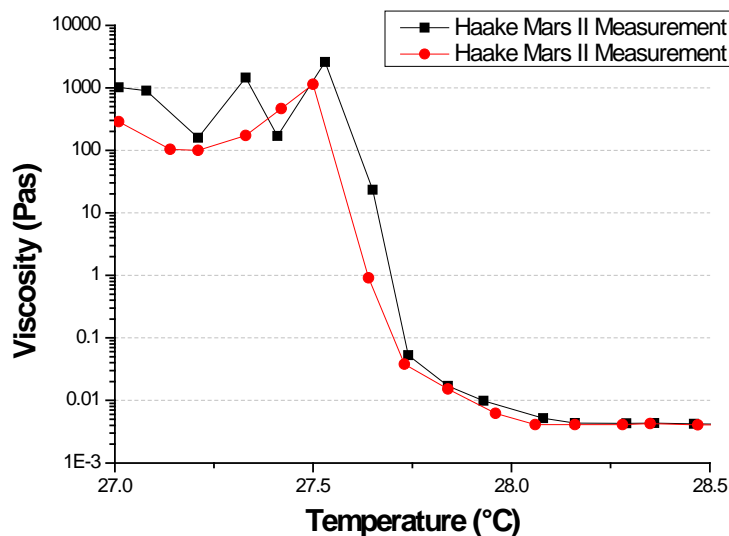


Figure 7. Oscillatory temperature steps. η' -T curves

Also, frequency sweeps at different temperatures have been accomplished. The obtained values (figure 8) at very low frequencies (that corresponds with materials at rest, about 0,01 Hz) are the same that at higher frequencies (1 Hz). So, if the Cox-Merz rule is accomplished, as it is explained below, it is not necessary to test at so low frequencies.

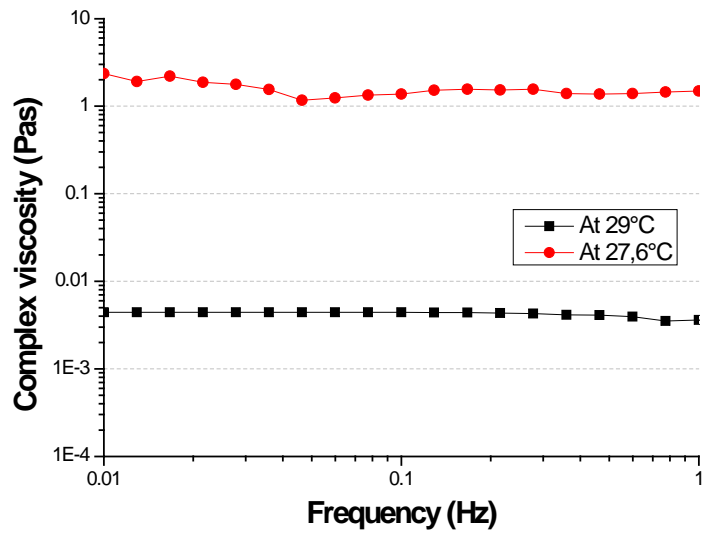


Figure 8. Frequency sweep at different temperatures. Stress=1 Pa

To finish with the rheological analysis of octadecane, in figure 9, the solidification and melting curves can be observed. In these curves, a slight hysteresis phenomenon can be observed.

To know if the values of complex viscosity can be extrapolated as values of viscosity, since the phase change can not be measured with the steady state flow, it is necessary to compare in the liquid phase the curve in steady state flow $\eta - \dot{\gamma}$ to the curve of the frequency sweep $\eta^* - \omega$. If these values fit well, it will be able to take the values of complex viscosity will be able to be taken during the phase change as viscosity values, as if the steady state flow curve had been obtained. This relation is known as the Cox-Merz rule [12]. In the figure 10, both curves are shown.

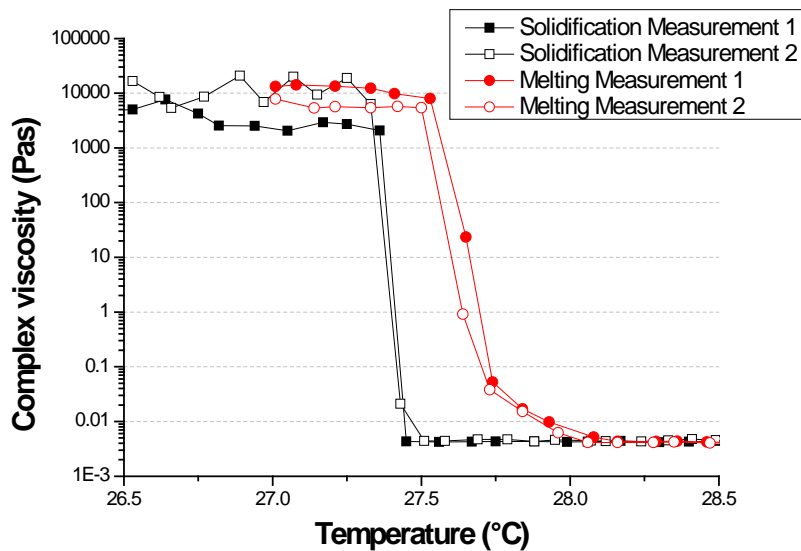


Figure 9. Comparison between the melting and the solidification curves. Frequency=1 Hz. Stress=10 Pa. Steps=0,1°C. Stabilization time=60 seconds.

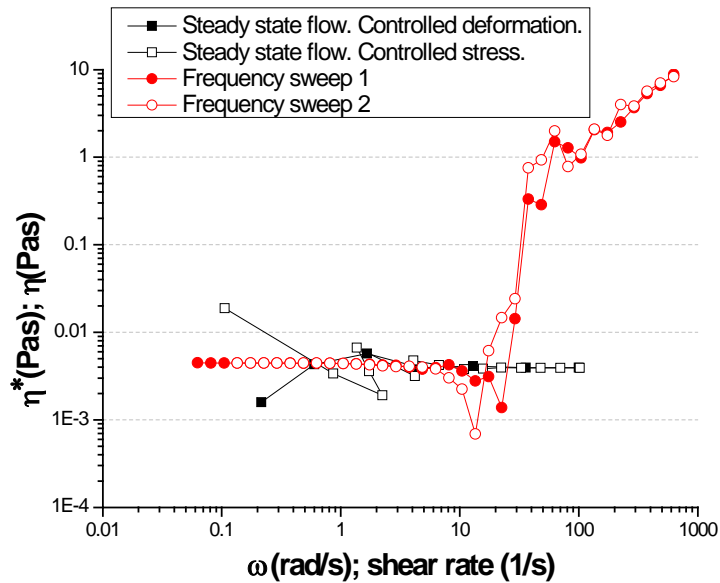


Figure 10. Comparison of the curves for the steady state flow and for the frequency sweep.

It can be observed that in the case of the steady state flow curves, they show a viscosity value about 4 mPas, with a shear rate value above 5 1/s. The measurements below a shear rate of 5 1/s show much noise. In the case of the frequency sweep curves, below an angular frequency of 5 rad/s they show a value of the complex viscosity about 4,4 mPas. Both values (4 and 4,4 mPas) are very close, however these values can not be compared in the whole range. In the frequency sweep, it is possible that above values 5 rad/s, there are problems of inertia that the rheometer can not correct. These problems are specially remarkable when working with substances of low viscosity, as for example in our case with the melted octadecane. In view of the results, it can be guaranteed that the Cox-Merz rule is accomplished.

4.1.2 Influence of the gap and of the heating and cooling rate on the measurement of the viscosity property

As the plate geometry has been used and therefore, it allows to control the gap of the sample, its influence on the results has been studied. In the same manner, the influence of the heating and cooling rate has been analysed. Due to the gradient between the sample temperature and the room temperature, and due to the low thermal conductivity of phase change materials, this aspect must be taken into account.

Two gap values have been tested, a high value about 1,4 mm and a low value about 0,4 mm. Regarding to the heating and cooling rates, rates from 2 to 0,1°C/min have been tested. Figure 11 and figure 12 show the obtained values of complex viscosity, both for the heating and cooling, and for the high and low gap respectively.

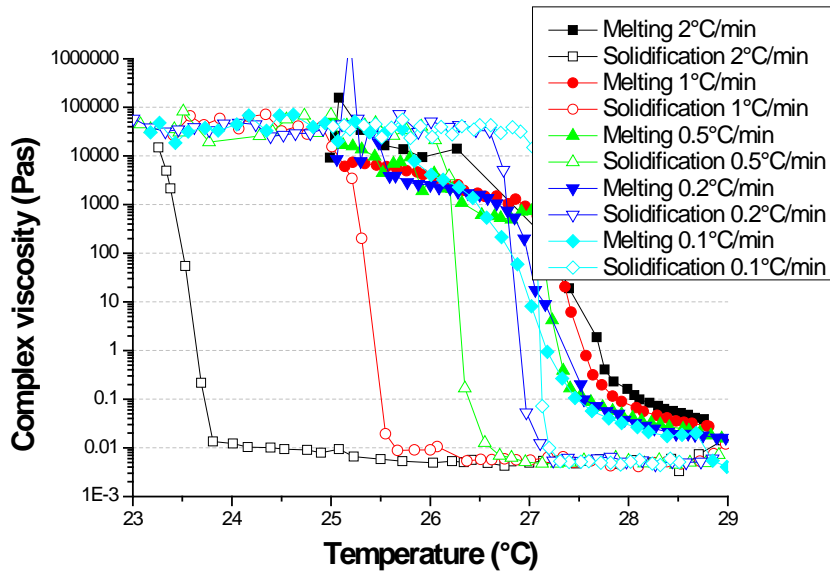


Figure 11. Melting and solidification curves with a gap of 1,4 mm for different heating and cooling rates. Frequency=1 Hz; Stress=1 Pa.

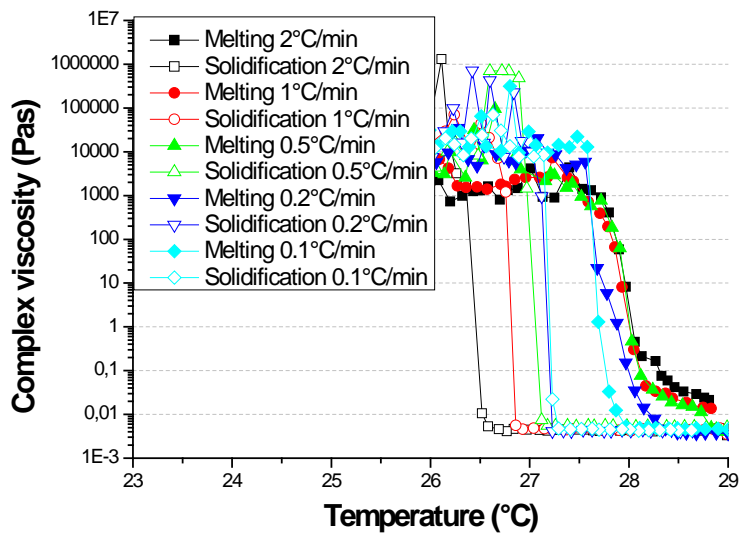


Figure 12. Melting and solidification curves with a gap of 0,4 mm for different heating and cooling rates. Frequency=1 Hz; Stress=1 Pa.

A higher apparent hysteresis between the melting and the solidification curves due to the method can be observed when working with higher gaps and with higher heating and cooling rates. The solidification temperature is displaced to lower temperatures, because the bigger size of the sample. Since the geometry at the beginning of the experiment will be at a temperature between the laboratory temperature and the setpoint temperature of the Peltier plate, the octadecane will start solidifying a first layer on the Peltier plate. In this way, for the same cooling rate, the geometry will take longer to see a solidified layer under itself. These differences are not so notable for the melting curves, perhaps because in this case, the lower part of the sample will be at a higher that its upper layer, helping the natural convection in the sample.

On the other hand, regarding to the heating and cooling rates, as it was expected, the hysteresis become bigger with higher heating and cooling rates, due to a lack of thermal equilibrium between the sample and the Peltier plate.

4.2 Analyzed substance: RT 16. Measurements with a PCM whose phase change temperature is lower than the room temperature

The main problem when measuring PCMs just as it was defined in the previous section, is the temperatures gradient inside the sample. The Peltier will be at the set temperature (around the phase change temperature), but at the beginning the geometry will be at the room temperature. This fact (in addition of the time that the sample will need to reach the thermal equilibrium in each moment) gives rise to wrong measurements on the rheological properties.

For this reason, a PCM with a phase change temperature lower than room temperature and a PCM with a phase change temperature higher than room temperature have been studied. Maybe in these cases, the optimum configuration would be another one completely different (an upper heated plate, an environmental test chamber, etc).

In the case of a PCM with a phase change temperature lower than room temperature, the organic PCM RT16 (that consists of a blend of paraffins) from the manufacturer Rubitherm has been chosen. The influence of the heating and cooling rate and the influence of the gap on the results have been analysed.

Regarding to the heating rate and cooling rate, in figure 13 it can be observed that at higher heating rates, the curve is displaced to the right side (to higher temperatures). On the other hand, at higher cooling rates the curve is displaces to the left side (to lower temperatures). This is due to a very high rate that makes sample be not in thermal equilibrium. For a heating and cooling rate of 0,1°C/min, the results do not have sense, since the solidification occurs at a higher temperature than the melting, with a difference about 1°C. Regarding to the gap, if the results of figure 13 and 14 are compared, the same behaviour is observed than in the case of octadecane.

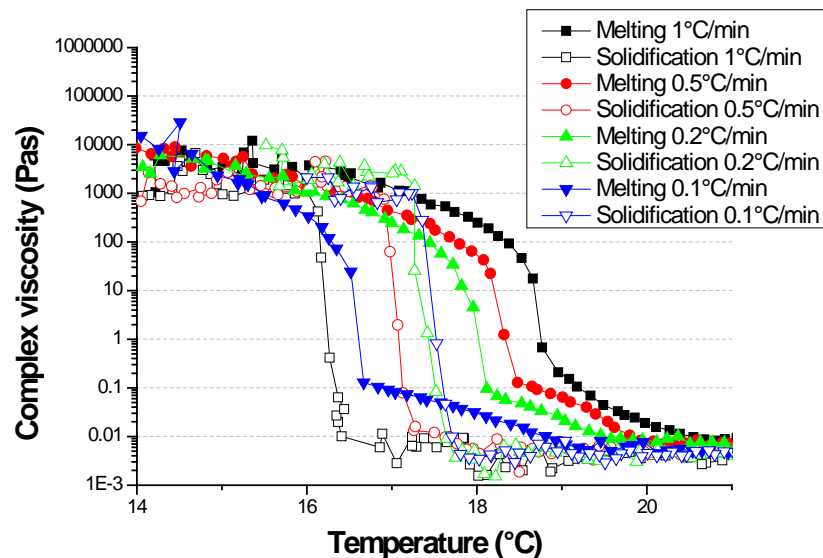


Figure 13. Melting and solidification curves with a gap of 0,9 mm for different heating and cooling rates. Frequency=1 Hz; Stress=1 Pa.

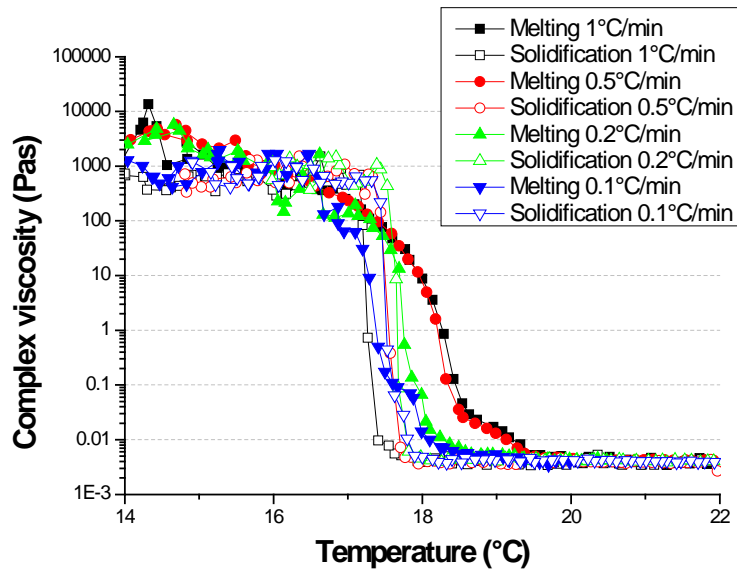


Figure 14. Melting and solidification curves with a gap of 0,3 mm for different heating and cooling rates. Frequency=1 Hz; Stress=1 Pa.

4.3 Analyzed substance: RT 90. Measurements with a PCM whose phase change temperature is higher than the room temperature

In this case an organic material from the manufacturer Rubitherm has been tested as well, specifically the product RT90 (the product is a blend of paraffins). In this case the differences in the results are more remarkable. Also the influence of the gap and of the heating and cooling rate on the results has been studied. However the results of the measurements do not show much repeatability. This lack of repeatability can be due to the higher gradient temperatures but it turns out to be very complicated to find a sense from the obtained results. For example in figure 15, it can be observed that with a higher gap, it seems that the PCM starts to melt at a lower temperature than for lower gaps. If an explanation to this phenomenon is tried to be found, and according to the visual phenomena observed, it can be stated that with higher gaps, the temperatures gradients is higher. So, the PCM near to the geometry will be at a lower temperature forming a solidified layer and the PCM near to the Peltier plate will be at a higher temperature forming a liquid layer. In this way the geometry together the solidified layer will oscillate over the liquid layer. In this way, the rheometer will find low resistance and therefore, the viscosity decreases abruptly although there is still a solidified layer.

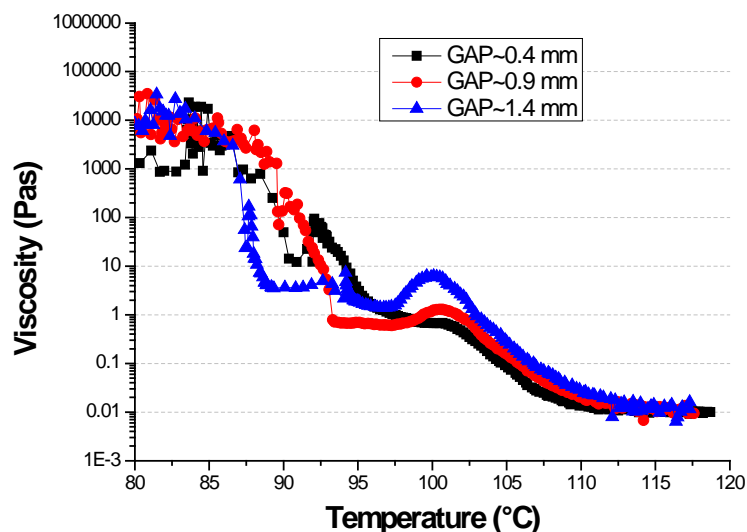


Figure 15. Influence of the gap on the Viscosity-Temperature curve. Frequency=1 Hz; Stress=0,5 Pa.

Also, it has been observed many peaks and noise in the obtained measurements. These peaks could be explained from the irregular shape of the solidified PCM layer. If the phase change temperatures range according to figure 15 (about 90-110°C) to the phase change temperature range obtained with a DSC are compared, it can be observed that the range has been displaced to higher values of temperature and this is wider. The explanation may be the temperature gradients.

However, the strange phenomenon is that in the case of solidification curves, in all the tests, the RT90 solidifies at the same temperature and the phase change temperatures range is very narrow, approximately at a set temperature about 90°C (see figure 16), independently of the gap and of the cooling rate.

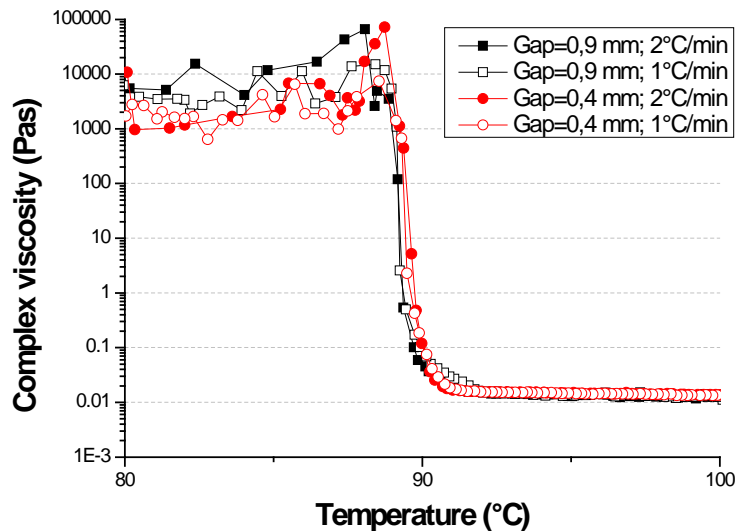


Figure 16. Solidification curves for different gaps and cooling rates. Frequency=1 Hz; Stress=0,5 Pa.

4.4 Analyzed substances: Phase change slurries

During the process of measurement in PCM slurries, one of the problems that takes place is the drying of the samples, due to their content of water. This problem affects to the sample, since the drying would make sample have a different composition. To avoid this drying, the equipment has a solvent trap, which let to cover the entire sample, and create an atmosphere saturated of water, avoiding the drying.

Figures 17 shows the time sweep for the sample (at 20°C), with the solvent trap and without it. Previous to these experiments, a strain sweep was accomplished, to know the linear viscoelastic region, in order to test always the sample within this range. A previous step to the time sweep has been to make a pre-shear of 100 1/s during 60 s, to see after if there is some structural change in the sample, and to start in this way always under the same conditions. However the time sweep does not show any structural change in the sample. If both curves are compared (figure 17), it can be observed that the sample covered by the solvent trap shows constant values of the G' and G'' modulus. On the contrary, the sample without solvent trap shows from 100 seconds a fast increase on these modules, due to the drying of the sample. Therefore, under these conditions of temperature the sample must always be tested with the sample covered by the solvent trap. This will avoid the drying of the sample.

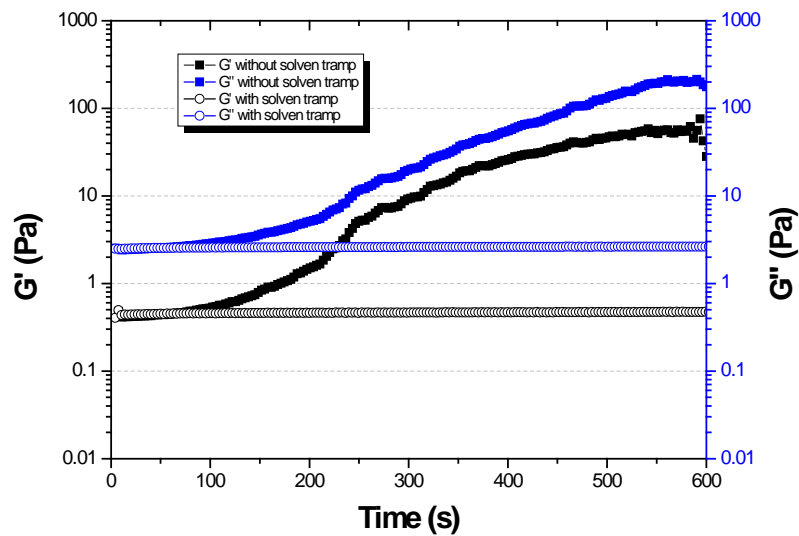


Figure 17. Time sweep with and without solvent trap. Frequency=1 Hz; Strain=0,1; Temperature=20°C

After the time sweep, the steady state flow curves for the phase change slurry have been obtained. The shear sweep has been accomplished by steps. According to the defined procedure, the rheometer takes the measurement as a valid measurement if the variation of the stress is lower than a 1% during at least 40 seconds. In case of not reaching the equilibrium, the rheometer takes the measurement as a valid measurement at 60 seconds. Under this procedure, the following curves shown in figure 18 have been obtained. A higher variation in the results is shown within the shear rate range from 0,001 to 0,1 1/s. Figure 19 shows the temperature ramp curve for the phase change slurry at a shear rate of 100 1/s and at a heating and cooling rate of 0,5°C/min. Regarding to this figure, the PCM in the slurry solidifies within the temperature range of 5-6°C and melts within the temperature range of 7,5-8,5°C approximately.

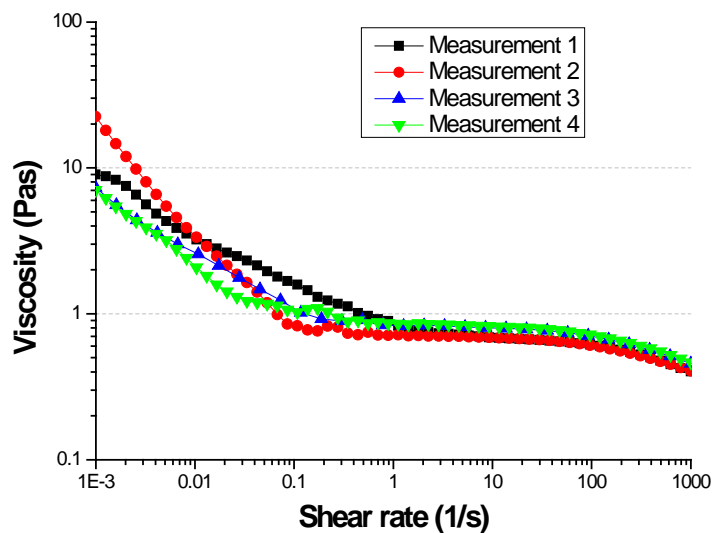


Figure 18. Steady state flow curve. Temperature=20°C

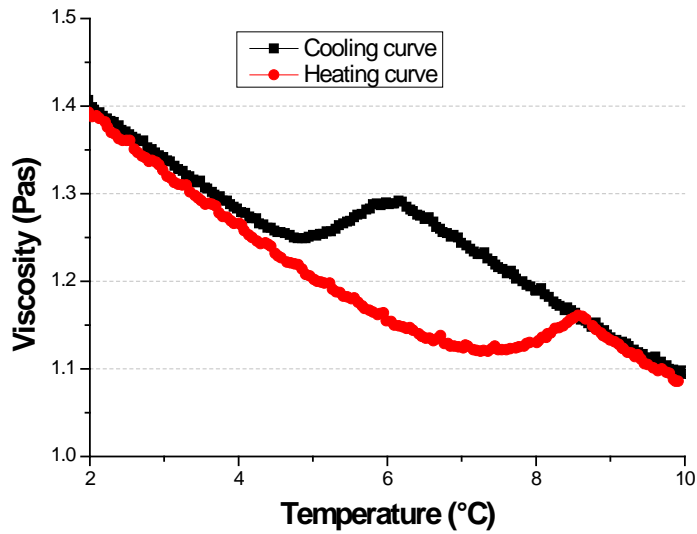


Figure 19. Viscosity-Temperature curve. Shear rate=100 1/s. Cooling and heating rate=0,5°C/min

4.4.1 Measurements of PCM slurries at high temperature

In the case of measuring PCM slurries at a temperature near to the room temperature, the use of the solvent trap can solve the problem of drying of the sample. The next step is to prove if the use of the solvent trap is also enough to avoid the drying when measuring at higher temperatures (in this case at 50°C). In spite of the fact that the sample has been prepared at 20°C and then it has been heated up, it is observed in the time sweep of figure 20 the drying of the sample. In view of these results, the time sweep has been carried out with the configuration of concentric cylinders having added a silicone oil on the sample. Due to the difference of density, the silicone oil will form an upper layer that will avoid the drying. As the volume of silicone oil regarding to the volume of the PCM slurry is very low, this will barely affect to the results. Figure 21 shows the time sweep with this configuration. It is observed that the sample is not dried. Figure 22 shows the flow curve for the slurry at 50°C with this configuration.

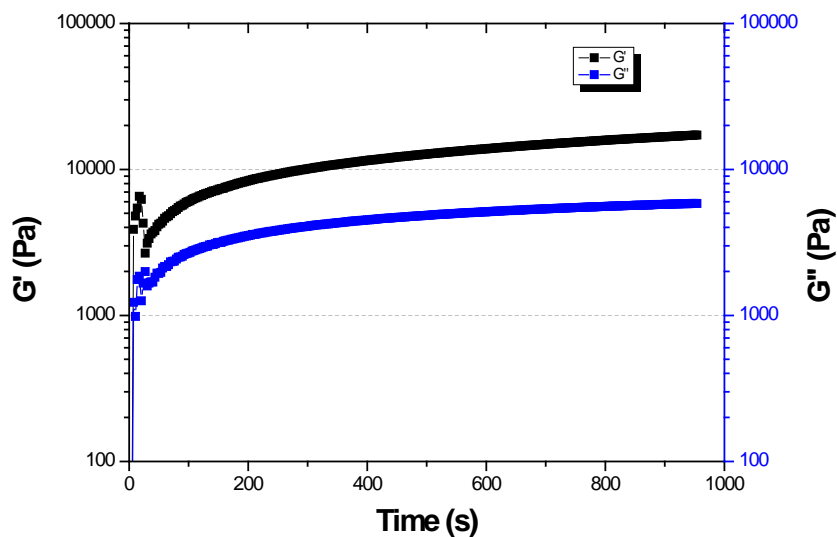


Figure 20. Time sweep for the PCM slurry at 50°C with plate-solvent trap. Frequency=1 Hz; Strain=0,1

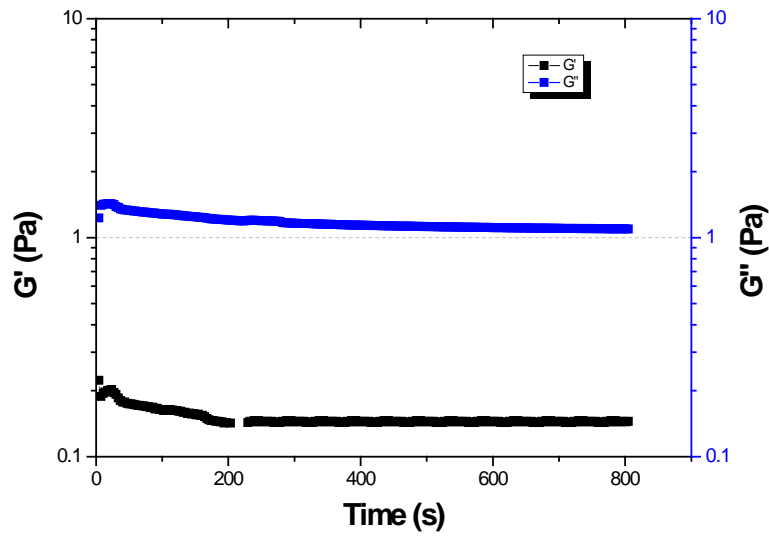


Figure 21. Time sweep for the PCM slurry at 50°C with concentric cylinders and silicone oil. Frequency=1 Hz; Strain=0,1

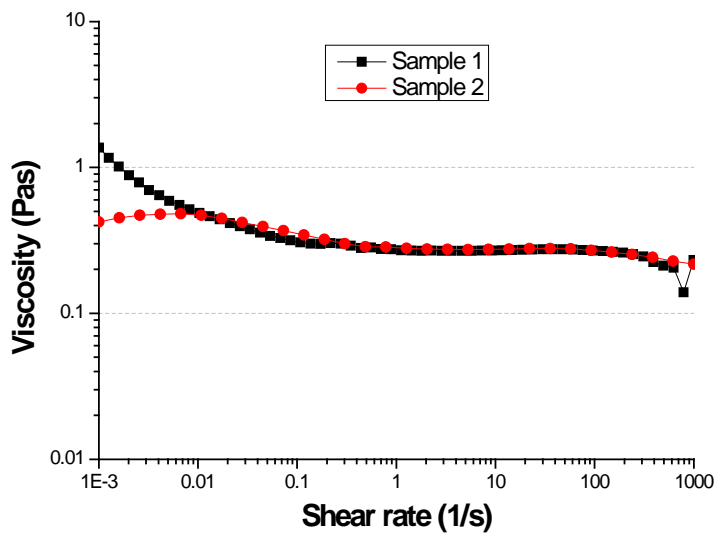


Figure 22. Flow curve for the PCM slurry at 50°C with concentric cylinders and silicone oil.

Also the time sweep and flow curves at 20°C with the configuration of plate-solvent trap (the sample did not dry) and with the configuration concentric cylinder-silicone oil (see figure 23) can be compared. The obtained values are almost the same. Regarding to the flow curves, the flow curves with both configurations at 20°C can be observed in figure 24. Important differences are observed for low shear rates.

With the concentric cylinders configuration, a temperature ramp has been tested. The problem is that it is only possible to obtain the viscosity-temperature curves at very low heating and cooling rates. The concentric cylinders are heated up or cooled down with a thermostatic bath, so the heating and cooling rate is very low and it is difficult to have during the experiment a constant rate.

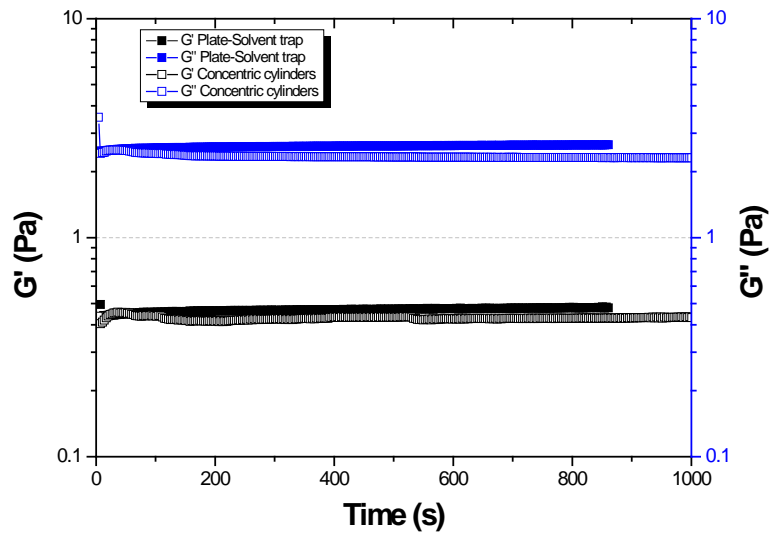


Figure 23. Comparison of the time sweeps with the geometry plate-solvent trap and concentric cylinders at 20°C. Frequency=1 Hz; Stress=1 Pa

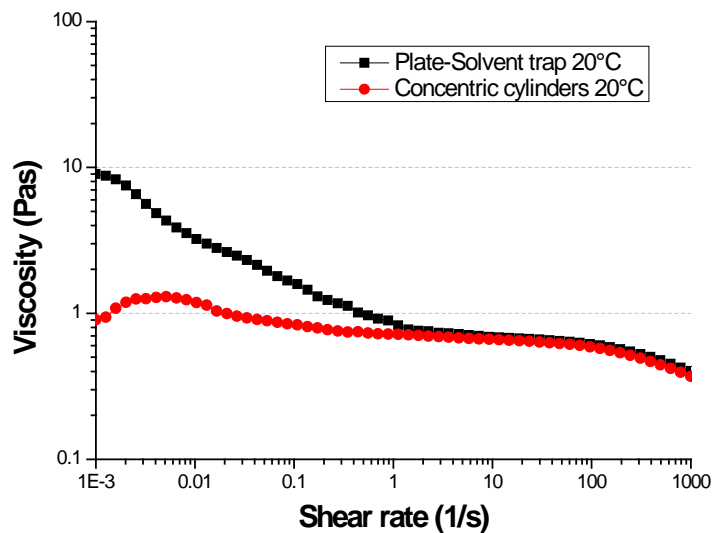


Figure 24. Comparison of the flow curves with the geometry plate-solvent trap and concentric cylinders at 20°C.

5. CONCLUSIONS

From the obtained results for PCMs, the main problem found when measuring the viscosity (or in this case the complex viscosity) is the temperature gradient in the sample and the lack of thermal equilibrium between the Peltier Plate and the sample, influencing the results. Perhaps the problem of the temperature gradient would be solved with the use of upper heated geometries. Nevertheless, neither Fraunhofer ISE nor University of Zaragoza has in their laboratories this kind of geometry. The option of repeating these measurements with the configuration of an experimental test chamber at University of Zaragoza is being considered, although it is known from experience, that PCM may leave the geometry due to the air flow that it is used to homogenize the temperature in the chamber.

According to the results presented in this report, a first draft of a measurement methodology is proposed.

5.1 Proposed methodology of measurement for PCMs

It seems clear that to obtain values of viscosity of PCMs during their liquid state and during the phase change, tests in oscillatory mode must be carried out. The steps to execute with a plate as geometry and a Peltier plate as temperature controller would be:

- 1) Strain or stress sweep at different temperatures (both in the liquid phase and during the phase change). A frequency about 1 Hz is advisable. With this step, the linear viscoelastic region will have been determined. For this first step, the Enthalpy-Temperature curve obtained previously with DSC can be helpful.
- 2) Frequency sweep at different temperatures (both in the liquid phase and during the phase change). The frequency sweep must be carried out at a stress or strain within the linear viscoelastic region (defined previously in step 1). Anyway it would be advisable to use a not very high stress or strain, so that it cannot affect to the measurement, but always working away from the resolution of the rheometer. This frequency sweep will provide information about the rheological behaviour of the sample (newtonian or non-newtonian, if the Cox-Merz rule is accomplished). If the sample is Newtonian, the step 3 will be able to be tested at any frequency. Frequencies below 1 Hz to avoid problems of inertia in the case of measuring with control stress rheometers.
- 3) Once the linear viscoelastic region determined and the frequency test executed, an oscillatory temperature ramp (or by steps) must be executed (both melting and solidification). If the PCM is not Newtonian, the test will be accomplished at 0,01 Hz and if the PCM is Newtonian at 1 Hz, it will be enough. Low gaps must be used to avoid temperature gradients in the sample. To choose the right heating and cooling rate, different rates should be tested, and select the heating and cooling rate from which the Complex viscosity-Temperature curve does not change.

In addition, the normal force during the test must be controlled. This must be always the same. The rheometer will adapt the gap as consequence of the phase change (as consequence of the volume change).

- 4) To know if the values of complex viscosity can be extrapolated of viscosity, since the phase change can not be measured with the steady state flow, the curve in steady state flow $\eta-\dot{\gamma}$ and the curve of the frequency sweep $\eta^*-\omega$ in the liquid state must be compared. If these values fit well, the values of complex viscosity will be able to be taken during the phase change as viscosity values, as if the steady state flow curve had been obtained (Cox-Merz rule).

Notes about the methodology: 1) The procedure above described is when working with a plate geometry and with the Peltier controller. Perhaps the plate is not the adequate geometry, due to the shear gradient across the sample. However, the cone does not allow to control the normal force, since the gap is set by the geometry itself. Regarding the temperature controller, it is possible that the use of an "environmental test chamber" would provide results more realistic with PCMs with a phase change temperature quite higher or quite lower than the room temperature, since this controller would avoid the temperatures gradient in the sample. Also the problem would be able to be solved with the combination of Peltier Plate and an upper heated plate. 2) If the PCM during its phase change or in its liquid phase is not a Newtonian fluid, it would be necessary to test the oscillatory temperature ramp at very low frequencies, about 0,01 Hz (PCM at rest). The problem in this case is that the rheometer needs at least one period to obtain a value of complex viscosity. If the frequency is 0,01 Hz, the rheometer would need at least 100 seconds. If the heating and cooling rate for example is 0,2°C/min, in these 100 seconds, the temperature will have vary about 0,34°C. In this way, the measurement would not be a right measurement due to so high variation in temperature. In this case, measurements at set temperatures should be carried out.

5.2 Proposed methodology of measurement for PCM slurries

In this case, a plate geometry also has been used. Although in these experiments, the control of the normal force is not necessary, a cone geometry has not been chosen because the gap must be at least 10 times higher than the maximum diameter of the droplets or capsules of PCM in suspension. The flowing of the droplets or microcapsules must be guaranteed. The following steps are proposed:

- 1) Strain or stress sweep at a temperature where the PCM is in its liquid or solid state. A frequency about 1 Hz is advisable. With this step, the linear viscoelastic region will have been determined.
- 2) Time sweep at a frequency of 1 Hz and at a stress or strain within the linear viscoelastic region (defined previously in step 1) during at least the time that the rotational test is going to take. Previously a pre-shear of 100 1/s during 60 seconds is carried out. If the temperature of the test is low (about or below the room temperature), the use of a solvent trap is advisable. If the temperature of the test is quite higher to the room temperature, the use of the concentric cylinder with an upper layer of silicone oil is advisable. In this way, the problem of the drying of the sample will be solved (the solvent of these kind of slurries is the water). The concentric cylinder would be able to be used in all the temperature range. However if a temperature ramp is carried out, the heating and cooling rate with this geometry will be established by the power of the thermostatic bath connected to it.
- 3) According to the time sweep, it will be known if the sample is dried during the test, and if the sample needs an equilibration time to rebuild its structure (in case of breakage of the structure). Then a steady state flow will be accomplished, from a shear rate of 0,001 to 1000 1/s. The steady state is reached when the variation of the measured stress during 40 seconds is lower than 1%. If the steady state is not reached in 60 seconds, a value is taken (integration time 10 s).

6. Future collaboration with host institution

From the work developed in the STSM these three months, future collaboration between the University of Zaragoza and Fraunhofer ISE will be conducted. In fact, this work is going to be completed with the reproduction of all the tests with the controlled stress rheometer that University of Zaragoza has in its properties determination laboratory. In addition, as future work, a hydrated salt will be measured.

7. Foreseen publications/articles resulting or to result from the STSM

In the 7th Experts Meeting for Annex 24-Task 42 "Compact Thermal Energy Storage: Material Development and System Integration", that will be celebrated 27-29 of March 2011 in Tokyo (Japan), this work will be presented. Moreover, I am editing with the collaboration of different researchers a paper from the work here presented.

8. Confirmation by the host institution of the successful execution of the STSM

Attached.

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