# RHEOLOGICAL BEHAVIOR OF SOYBEAN BIODIESEL AT LOW TEMPERATURES

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*Abstract. The importance of biodiesel fuels as a renewable energy resource has been growing fast over the last years due to its many advantages over petroleum fuels, such as low toxicity, low $CO_2$ emission, and higher lubricity and biodegradability. However, its main disadvantage is related to the poor cold flow properties. At low temperatures, wax crystallizes and gives rise to a gelation process that may lead to plugging of filters and lines. Although this consists a major problem for the use of biodiesel as fuels, little has been done in order to investigate the rheological behavior of these materials at low temperatures.*

*In this paper, the rheological characterization of soybean biodiesel is performed under the guidelines of a recently proposed protocol for waxy crude oils (Marchesini et al., 2012), which possesses a similar behavior at low temperatures. We present a set of preliminary results, including thermal cycle, constant shear stress and oscillatory tests.*

*Keywords: rheology, biodiesel, rheometry, low temperature, flow properties*

## 1. INTRODUCTION

Biodiesel is a renewable and biodegradable fuel. It derivates from animal fats or from vegetable oils such as soybean, castor, palm, sunflower and peanuts. It is mostly produced by a chemical process named transesterification with short-chain alcohols, such as methanol or ethanol (Graboski and McCormick (1998); Pinto *et al.* (2005); Moser (2009)). Biodiesel can be used in any diesel engine and today is still usually mixed with fossil fuels.

Currently, due to the global effort for sustainability, biodiesel appears as a very good option to petroleum oil, which is known to be a non-renewable source of energy. The use of biodiesel can reduce dependency on oil fuels and contributes greatly to a decrease in air pollution.

Despite being a great alternative source of energy, biodiesel brings an already existing problem in petroleum oils, which occurs because of the wax crystallization: the difficulty of using it at low temperatures. In this case, biodiesel's flow becomes complicated and the cross section of pipelines starts to be reduced according to the wax deposit.

At low temperatures biodiesel turns into a Non-Newtonian fluid, starting to behave in a complex way characterized by a sharp increase in viscosity. The flow properties are dependent on the temperature and shear histories during the cooling process, rendering the rheological characterization rather difficult. Although this consists a major problem for the use of biodiesel as fuels, little has been done in order to investigate the rheological behavior of these materials at low temperatures (Conceição *et al.* (2005); Goodrum *et al.* (2003); Santos *et al.* (2011)). Therefore, a lot of investigation and improvement in the study of rheological biodiesel behavior is still required.

Hence, we have developed this research, using soybean biodiesel samples and following the procedure recommended by Marchesini *et al.* (2012) for waxy crude oils.
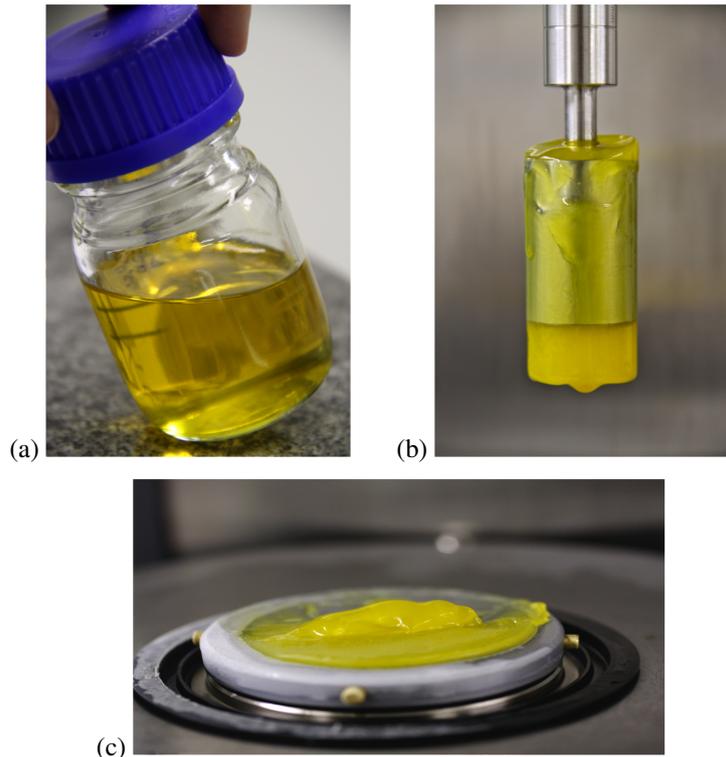
Figure 1. (a) Biodiesel at room temperature ($\approx 23°C$); (b) and (c) Gelled soybean biodiesel after an experiment on a DIN bob and parallel plate geometries, respectively.

## 2. THE EXPERIMENTS

To study the rheological behavior of soybean biodiesel, an ARES-G2 rheometer from TA Instruments was used with two different geometries: smooth parallel plates, 60mm diameter with gaps within 0.25 and 3.0mm and DIN Concentric Cylinder, gap 1.05mm.

In order to prepare the sample first one of the bottles containing the biodiesel is homogenized. Secondly a sample is collected from the bottle and loaded into the rheometer with a syringe. The sample is placed between the plates or in the cup at $25^oC$. Then the rheometer temperature is raised to the initial temperature $T_i$ which is maintained for 15 minutes until the sample is stabilized. Thereby the thermal memory is erased.

A set of thermal cycle tests was performed to figure out the relation between viscosity and temperature. In these tests, an initial temperature ($T_i$) is imposed to the sample, which is then cooled down at a fixed cooling rate ($\dot{T}_h$) at a constant shear rate ($\dot{\gamma}_h$), until a pre-determined final temperature ($T_f$) is reached. Immediately afterwards, the ramp is reverted and the sample is reheated back to the initial temperature.
The main parameters of a thermal cycle test are indicated in Fig. 2 below:

Starting at $T_i$ and following the cycle path indicated by the arrows in Fig. 2, it is seen that initially the viscosity increases mildly with temperature up to the crystallization temperature $T_c$, displaying the typical Arrhenius temperature dependence. In fact, a Newtonian behavior is always observed in this range. Beyond (below) $T_c$, a dramatic increase in viscosity takes place due to the gelation of the material.

Below the *WAT*, new wax crystals precipitate and the already existing ones grow, as the temperature is decreased. Both the solid fraction and length distribution, are then increased, contributing to build up a structure that is formed by the interaction between wax crystals.

As previously mentioned, at $T_c$ the minimum amount of wax crystals for gelation is achieved, causing a sharp change in the slope of the viscosity-temperature curve. Thus, below $T_c$ the rheological behavior of waxy oils becomes non-
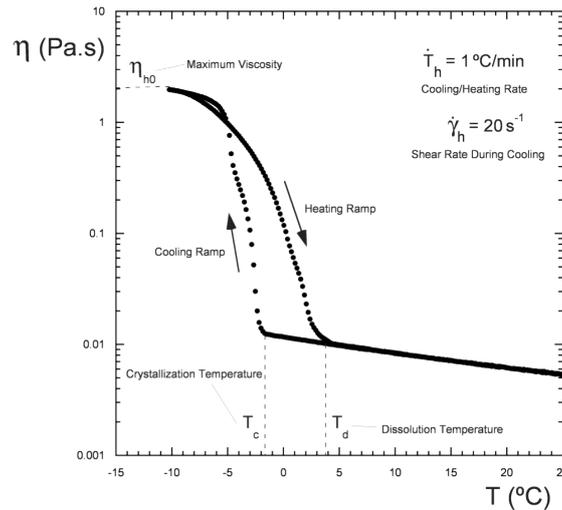
Figure 2. Main parameters of a thermal cycle test.

Newtonian, and becomes dependent on the shear and temperature histories experienced by the oil sample, in addition to the dependence on the present shear rate, time of shear, and temperature like most non-Newtonian materials.

The upper portion of the thermal cycle pertains to the heating ramp. Firstly it is interesting to note that the viscosity reaches its maximum, $\eta_{h0}$, at a temperature that is slightly above $T_0$. This is due to a time lag between the imposed and the actual sample temperature. That is, at a given instant of time during the test, the sample temperature is not exactly coincident with the imposed temperature, due to the thermal inertia of the system. Past $\eta_{h0}$, the viscosity decreases as the sample is heated, since the wax crystals start to dissolve. At a given point along the heating portion of the loop, the dissolution temperature $T_d$ is achieved, above which the Newtonian behavior of the oil is restored.

## 3. RESULTS

### 3.1 Testing conditions

The influence of the initial temperature was investigated. To this end some thermal cycle tests were performed with $T_i$ being 25°C, 50°C and 80°C. The results are summarized in Fig. 3(a).



(a)

(b)
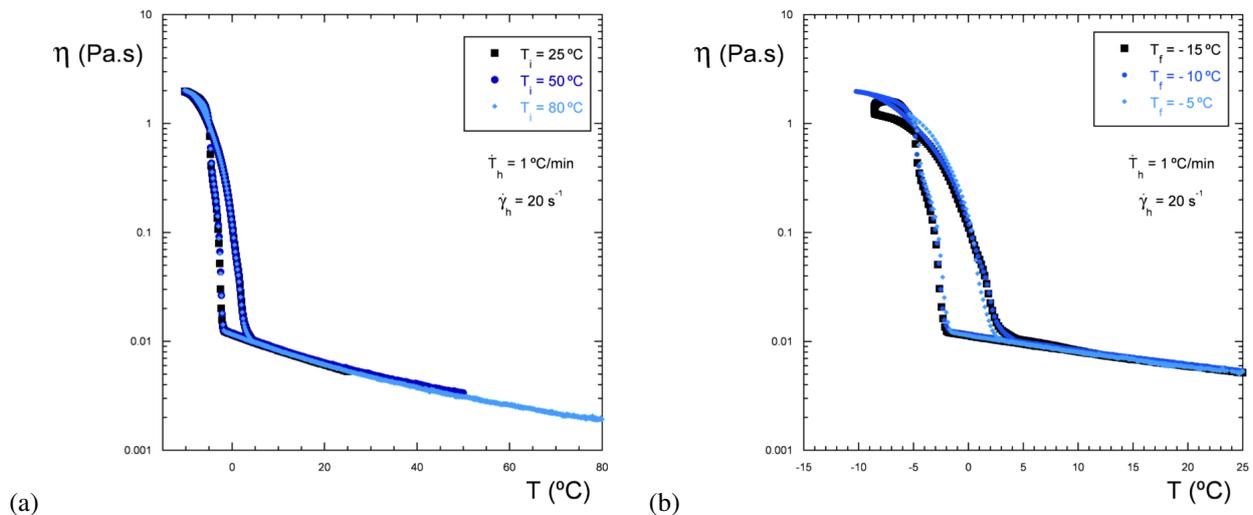
Figure 3. (a) Effect of initial temperature $T_f$; (b) Effect of final temperature $T_f$.

Since $\eta_{h0}$ did not show any dependency on $T_i$, 25°Cwas imposed for all subsequent thermal cycle tests.

The influence of the final temperature was also investigated (Fig.3(b)). $T_f$ varied: initially -15°Cwas applied, following -10°Cand then -5°C. Since -10°Cis the lowest temperature the rheometer ARES-G2 is able to achieve and maintain, the final temperature was chosen to be equal to $-10^oC$.

A triple thermal cycle shown in Fig. 4(a) implies that the composition does not change throughout testing. It consists of using the same sample to perform three followed thermal cycles.
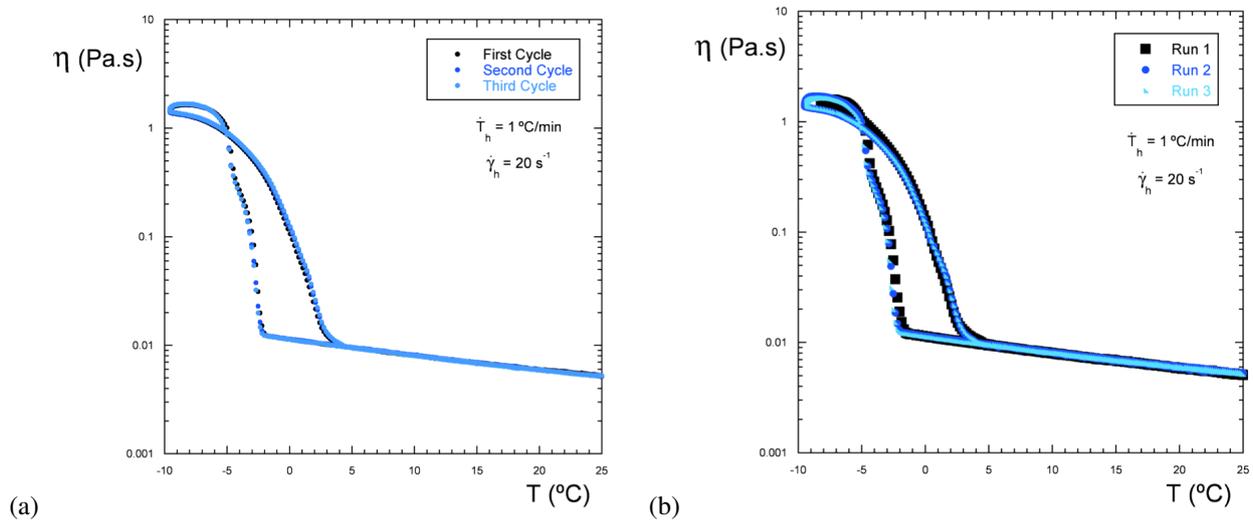


Figure 4. (a) Triple thermal cycle test; (b) Repeatability.

The results show that the three curves, each one pertaining to one cycle, are coincident. This implies that sample composition does not change throughout testing.

Repeatability was investigated by comparing three different runs, i.e. using different samples, of the same rheometric test. The results are presented in Fig. 4(b). As the three curves, each one being correspondent to one run, are essentially equal, we can conclude that the tests present a very good repeatability.

The results for different geometries were also compared and are shown in Fig. 5(a). Smooth and cross hatched parallel plates, concentric and recessed end concentric cylinders, and cone and plate geometries were tested.
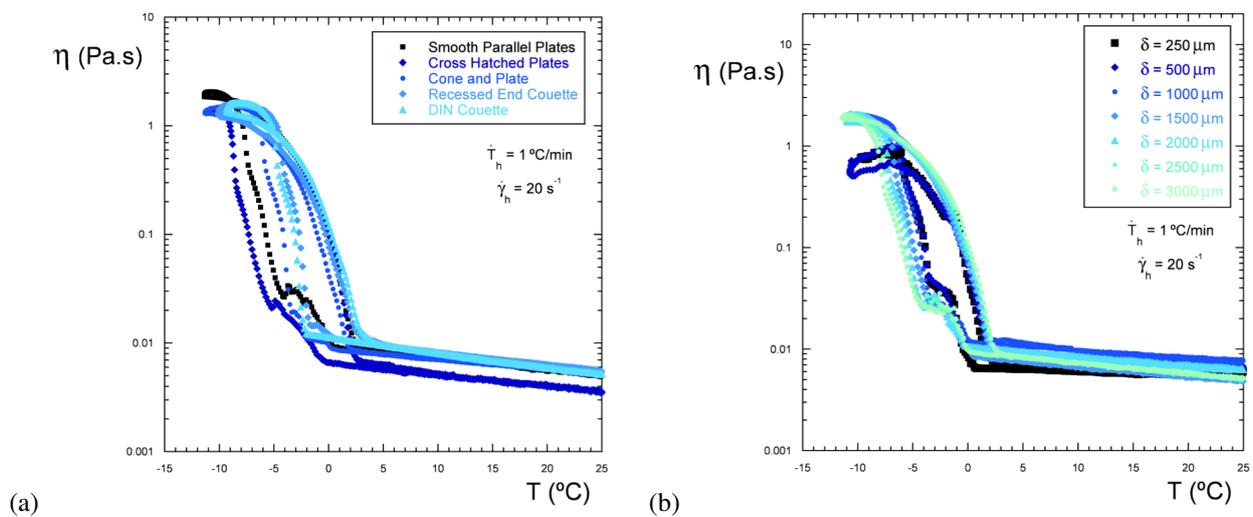


Figure 5. (a) Effect of geometry; (b) Effect of gap ($\delta$).

Fig. 5(a) illustrates how different geometries give rise to different results. Comparing all of them the DIN Couette geometry seems to give the most reliable results. Since soybean biodiesel has very low viscosity at room temperature, the concentric cylinder geometry is more appropriate because of the lower torques it can achieve at this portion of the curve. Moreover, It is the only curve in which it is possible to identify a crystallization temperature $T_c$.

The next step was to investigate if the gap $\delta$ of the DIN concentric cylinder is large enough to ensure reliable data, as discussed elsewhere Marchesini *et al.* (2012). Smooth parallel plates were used for this purpose, since varying the gap in a cylinder geometry is rather difficult. The gap was varied from 250 to $3000\mu$m. The results are summarized in Fig. 5(b).

It is possible to observe that results for the two smallest gaps, namely $250\mu$m and $500\mu$m, give rise to curves with shapes considerably different than for larger gaps, specially at the low temperature range. Moreover, the curves pertaining to the other gaps are essentially coincident. Hence, these results illustrates that the gap ($\delta$) must be large enough to ensure reliable data. The gap can not be $\approx 10$ times smaller than the size of the wax crystals/aggregates or it will not be possible to produce gap-independent results.

## 3.2 Cooling process

The cooling process, determined by cooling rate $\dot{T}_h$ and shear rate during cooling $\dot{\gamma}_h$, was also investigated. Thermal cycles varying each parameter individually are displayed in Fig. 6. To investigate the influence of the shear rate during cooling, $\dot{T}_h$ was fixed at 1°C/min, as shown in Fig. 6(a). On the other hand, Fig. 6(b) shows the influence of the cooling rate by keeping $\dot{\gamma}_h$ constant at a value of $20s^{-1}$.



(a)

(b)
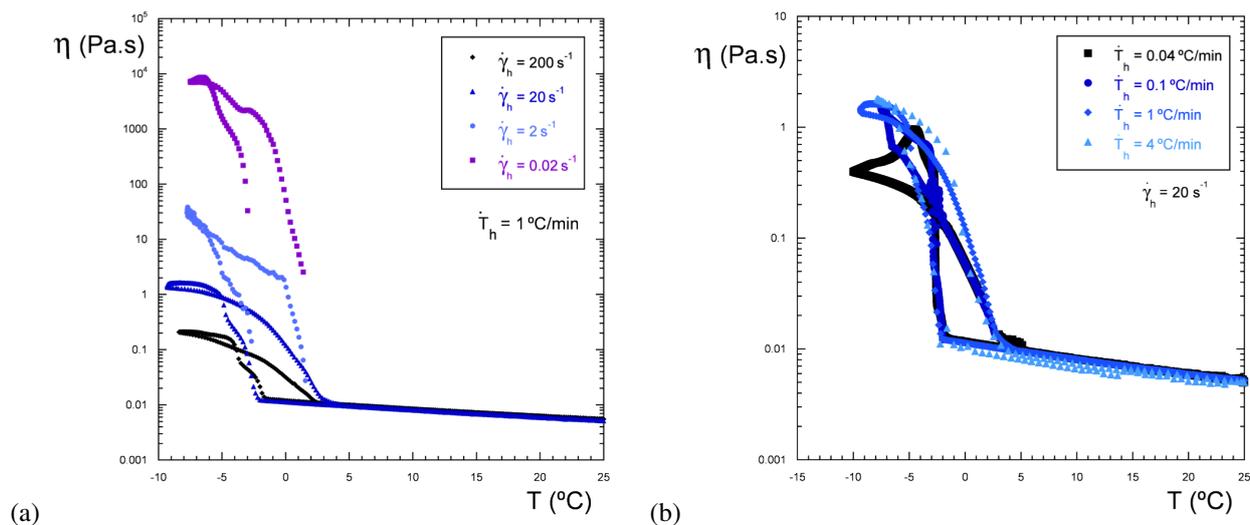
Figure 6. (a) Effect of shear rate during cooling $\dot{\gamma}_h$, (b) Effect of cooling rate $\dot{T}_h$.

It becomes evident that the shear rate applied during cooling has a much more pronounced effect on the rheology than the cooling rate. Fig. 6(a) shows that the viscosity at the lowest temperature, $\eta_{h0}$, varies orders of magnitude depending on the shear rate applied. Also, $\eta_{h0}$ is much higher for lower $\dot{\gamma}_h$'s. Curiously, $T_c$ is apparently not altered by the cooling conditions. On the other hand, $\dot{T}_h$ has minor effect on biodiesel rheology. At the present time, no explanation for the different behavior observed in the curve corresponding to 0.04°C/min could be given.

## 3.3 Postcooling flow properties

Postcooling flow properties refer to the rheological properties of the oil after the sample has been cooled down to the measurement temperature, in this case equal to -10°C (unless specified otherwise). This means that every result presented next is obtained after the sample is submitted to a temperature ramp, under fixed $\dot{T}_h$ and $\dot{\gamma}_h$ - which are always indicated in the plots.

### 3.3.1 Flow Curves

Flow curves were performed at different temperatures do illustrate the onset of non-Newtonian behavior. Samples were statically cooled ($\dot{\gamma}_h= 0s^{-1}$) at a cooling rate of 1°C/min. Results are plotted in terms of viscosity vs. shear rate (Fig. 7(a)) as well as shear stress vs. shear rate (Fig. 7(b)).
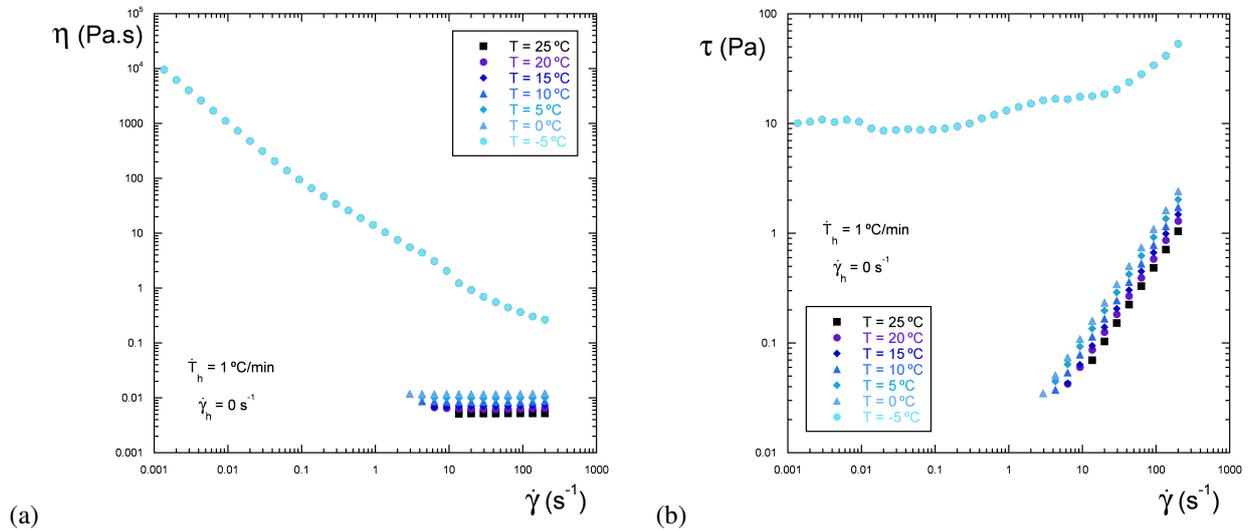


Figure 7. Flow curves performed at different temperatures; (a) $\eta$ vs. $\dot{\gamma}$ and (b) $\tau$ vs. $\dot{\gamma}$.

It is clear that soybean biodiesel is Newtonian at temperatures above 0°C, but displays a highly non-Newtonian behavior at the temperature of -5°C. This fact is consistent with the previously presented results, since the thermal cycle tests indicated that $T_c$ (temperature at which a sharp increase in viscosity is observed) is $\approx$ -2°C.

### 3.3.2 Oscillatory tests

Strain sweep tests were performed to investigate the elasticity of the gelled material. Fig.8 displays oscillatory experiments under different cooling conditions: Fig. 8(a) shows the influence of $\dot{\gamma}_h$, whereas Fig. 8(b) presents results of the variation of cooling rate. G' (elastic modulus) is represented by the filled marks, while empty marks are used for G" (loss/viscous modulus).
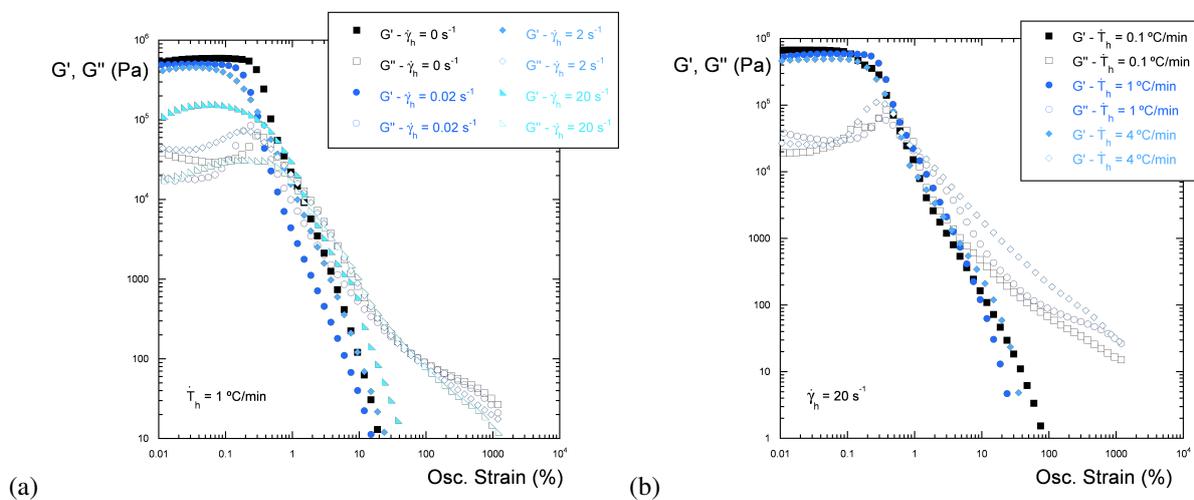


Figure 8. Strain sweep tests: Effect of shear rate during cooling $\dot{\gamma}_h$, (b) Effect of cooling rate $\dot{T}_h$.

G' is higher than G" for all cases investigated, meaning that the gel is fully structured at low % strain. Also, the viscoelastic linear region is rather short for all cases investigated. Yielding of the material, i.e. onset of flow, starts at $\approx$ 1% strain. Once again, it was observed that varying the cooling rate (Fig. 8(b)) did not significantly alter the rheological behavior of gelled biodiesel. Variation of $\dot{\gamma}_h$ ((Fig. 8(a))) led to different behavior only for the highest $\dot{\gamma}_h$ applied ($20 s^{-1}$): G' does not reach its maximum level. This is due to the breakdown of the structure caused by (strong) shearing of the sample.

## 4. CONCLUSIONS

Some testing conditions for the rheological characterization of soybean biodiesel were established. Effects of $T_i$, $T_f$, geometry, and gap were investigated. The results showed good repeatability and negligible compositional changes during thermal cycling. The shear rate applied during cooling $\dot{\gamma}_h$ drastically changes $\eta_{h0}$, whereas the cooling rate $\dot{T}_h$ seems to have minor effects on biodiesel rheology. In the flow curve results Non-Newtonian behavior is clearly observed in tests performed at a temperature below $T_c$. Strain sweeps show that moderate shear rates during cooling do affect the gelation process. These tests also indicate that the cooling rate does not alter significantly the rheology.

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