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# Thermal fatigue and collapse of waxy suspensions

Diogo E. V. Andrade<sup>1,2</sup> · Philippe Coussot<sup>1</sup>

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## Abstract

Due to the existence of a continuous (percolating) network of weak interparticle bonds in a liquid, wax suspensions can behave as “soft breakable (brittle) solids”: under the action of either a large stress over a short time or oscillating low stress (fatigue test), the initially solid network of these materials is broken and dispersed in the liquid, which turns them into abruptly (“collapse”) and irreversibly to a low viscous fluid. Here we show that the rheological behavior of these materials is not only impacted by the temperature but also by the history of the temperature. The elastic modulus and the yield stress increase when the temperature is decreased, and the data for different concentrations (ranging from 7 to 50 wt% of wax in oil) and temperatures as a function of the distance to the critical temperature associated with the transition to liquid state, fall along a master curve, which shows some equivalence between temperature and concentration. More surprisingly, the elastic modulus in the linear regime and the yield stress are dependent on the minimum temperature the material has experienced during its preparation. As a consequence of these different characteristics, an original rheological behavior so far essentially observed with very different materials (metals) results, namely *thermal fatigue*: when the material is submitted to temperature cycling (small temperature amplitude test), the material progressively weakens during each elementary thermal cycle and can finally “collapse” after a sufficient number of cycles, i.e., the elastic modulus in the linear regime decreases from  $10^6$  to  $10^3$  Pa. These findings could have implications in the start-up flow of waxy oils in pipelines since with the help of this technique, the material strength (e.g., the yield stress) and consequently the pressure required to resume the flow can be reduced considerably just by imposing thermal cycles.

**Keywords** Waxy suspensions · Brittle solids · Thermal cracking · Thermal fatigue

## Introduction

The production and transportation of waxy crude oil is a challenge in offshore scenarios. The crude oils, that experience high temperatures in the reservoirs, are submitted to low temperatures during the transportation by pipelines, which are in contact with the seabed at around 4 °C (Smith and Ramsden 1978; Huang et al. 2011). During the flow in the pipelines, the oil loses heat to the environment and at a given temperature—called WAT (wax appearance temperature)—the heaviest

normal hydrocarbon molecules precipitate out in the solution as crystal structures (Paso et al. 2005). At high temperatures, the crude oils behave as Newtonian fluids (Wardhaugh and Boger 1991; Venkatesan et al. 2005), whereas, below the WAT, the solid crystals precipitated in the solution are responsible for three main issues in the production process: (i) the crystals give a non-Newtonian behavior to the material increasing the material viscosity and, as a consequence, the required pumping power to keep the flow also increases (Marchesini et al. 2012); (ii) these solids wax can deposit in the inner surface of the pipelines, in these cases, the PIG (pipeline inspection gauges) must be used to remove the paraffin deposited and the deposition rate must be known in order to determine the wax pigging frequency (Aijejina et al. 2011); (iii) when the flow is interrupted, the crystals can entrap the oil and yield a solid-like structure to the material, in this case, one must know the strength of the solid structure after the stoppage in order to determine the required pressure to break down the structured material and to resume the flow (Visintin et al. 2005a).

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The knowledge of the rheological behavior of waxy oil is fundamental to design the pumps and the pipelines and to improve the production and transportation process. Although extensive research has been conducted over the past five decades, there are many points regarding the rheological behavior that are not clear in the literature. The majority of the authors agree that these materials present a yield stress at low temperatures, in the sense that after resting for some time, it is necessary a stress larger than a minimum stress to restart the flow. Some authors say that waxy oils are thixotropic materials (Visintin et al. 2005b; de Souza Mendes and Thompson 2012; Teng and Zhang 2013; Dimitriou and McKinley 2014) while others state that waxy oils must be understood as irreversible time-dependent materials since after the shear, the material does not completely recover the viscosity when the applied shear rate is decreased and does not recover the initial solid-like structure at rest (Rønningsen 1992, 2012; Mendes et al. 2015; Andrade and Coussot 2019).

It is well known that waxy oils are thermal and shear-history dependent (Wardhaugh and Boger 1987). In other words, the different temperatures, cooling rates, and shear applied in the material during the cooling interfere in the crystallization process (nucleation and crystals growth), affecting the morphology of the crystals (Rønningsen et al. 1991; Paso et al. 2005; Yi and Zhang 2011; Andrade et al. 2018) and, as a consequence, influence the macroscopic behavior of the waxy oil at the end of the cooling. The thermal and shear histories are usually evaluated by varying the initial (Smith and Ramsden 1978; Marchesini et al. 2012; Jemmett et al. 2013; Andrade et al. 2015; Dalla et al. 2019) and the final (Davenport and Somper 1971; Hou and Zhang 2010; Mendes et al. 2017) temperature of the cooling, the cooling rate (Lee et al. 2008; Mendes et al. 2017; Andrade et al. 2018), the applied shear during cooling (Venkatesan et al. 2005; Lin et al. 2011; Mendes et al. 2017), and the resting time at the final temperature (Wardhaugh and Boger 1991; Chang et al. 2000; Silva and Coutinho 2004; Mendes et al. 2017). As a general conclusion, it seems that decreasing the final temperature, or increasing the concentration of wax, the material yield stress increases because under these conditions more crystals are formed; the resting time may play a role depending on the composition of the oil, in other words, it seems that for the majority of the crude oils, increasing the resting time at the final temperature increases the strength of the structure (Lin et al. 2011; Van Der Geest et al. 2019); on the other hand, for model waxy oils, the material strength varies in the first minutes of rest and then the elastic modulus and the material yield stress become independent on the resting time (Andrade and Coussot 2019); regarding the dynamic cooling, the final structure of the material is much affected by the shear during the cooling, i.e., the material strength (elastic modulus and yield stress) after dynamic cooling is order of magnitudes lower than the strength of the material obtained after static

cooling (Lin et al. 2011; Andrade et al. 2015). Finally, it is interesting to note a non-monotonic variation of the strength of waxy oils in the solid regime as a function of the initial cooling temperature (Marchesini et al. 2012; Andrade et al. 2015; Dalla et al. 2019), the cooling rate (Lee et al. 2008; Andrade et al. 2018), and the shear stress applied during the cooling (Venkatesan et al. 2005).

Here we intend to clarify the impact of thermal changes on waxy crude by focusing on a model system. These materials are commonly used as model materials to study the rheological behavior of waxy crude oil (Singh et al. 2001; Dimitriou et al. 2011; Zhao et al. 2012; Mendes et al. 2015; Andrade et al. 2017) that are transported in subsea pipelines, lubricating mineral oil (Webber 1999, 2001) which can reach low temperatures in some applications, and in a recent study (Andrade and Coussot 2019), it was also proposed that model waxy oils might be used as a model system to simulate and explain natural catastrophic events such as landslides and avalanches.

Although we cannot claim that this material behaves exactly as a typical waxy crude, it can be expected that some fundamental qualitative aspects of the behavior of the model wax suspensions will be found also with waxy crude oils, since both material types are basically made of waxy matter in suspension in a liquid and which crystallize progressively as the temperature is decreased. Moreover, the use of these simple model systems might make it possible to distinguish more easily the original trends of these systems without being too much blurred by various complications due to some additional components.

Model waxy oils are systems composed of paraffin wax mixed in mineral oil. As mentioned previously, these materials behave as a Newtonian fluid at high temperatures, when all the paraffins are dissolved in the oil, and below the WAT, the paraffins precipitate in the oil as wax crystals giving a non-Newtonian behavior to the material. In a previous study (Andrade and Coussot 2019), it was shown that, when cooled at rest (without external stress perturbation in the sample during the cooling), such a material type may be seen as a brittle solid presenting very high elastic modulus (up to  $10^6$  Pa) and very low critical strain (in the order of  $5 \cdot 10^{-5}$ ) around which the material leaves the linear regime, and finally the material transforms into a simple liquid after some significant shear (Andrade and Coussot 2019). The impact of concentration at a given temperature was analyzed, suggesting that during cooling, the crystals formed are connected by interparticle solid bonds that structure the sample and give the solid-like behavior to the material. Here we intend to analyze how the thermal history impacts these properties.

We first recall in more detail the main characteristics of the material used. Then we further analyze the influence of the temperature in the solid regime of the waxy model oil: we demonstrate that the elastic modulus variations when the temperature decreases at a given concentration are similar to its

163 variations when the concentration is increased at a given tem- 209  
164 perature. It is then shown that the waxy oil presents a thermal 210  
165 memory in the sense that the elastic modulus in the linear 211  
166 regime and the yield stress are dependent on the minimum 212  
167 temperature the material has experienced. Finally, a thermal 213  
168 fatigue test (small temperature amplitude tests) may be used to 214  
169 strongly alter the material, as for metals (Starling and Branco 215  
170 1997; Persson et al. 2005) and bitumen (Soenen and 216  
171 Vanelstraete 2003; Kumar-Das et al. 2012), but here this leads 217  
172 to the liquefaction of the material. We start with the experi- 218  
173 mental section, followed by the results, discussion, and then 219  
174 the main conclusions. 220

## 175 Experimental section

176 The model wax oils analyzed are composed of a paraffin wax 225  
177 (Sigma Aldrich 327212 CAS-No:8002-74-2, with a melting 226  
178 point between 58 and 62 °C) mixed in a mineral oil (Sigma 227  
179 Aldrich 330779 CAS-No: 8042-47-5) as proposed in previous 228  
180 studies (Dimitriou et al. 2011; Mendes et al. 2015; Andrade 229  
181 et al. 2018; Andrade and Coussot 2019). The samples were 230  
182 stored in an oven at 60 °C, a temperature higher than the solid- 231  
183 liquid equilibrium temperature for these materials. It is worth 232  
184 remembering that when mixed in the mineral oil, the wax 233  
185 solubilizes in the liquid and the thermodynamic solid-liquid 234  
186 equilibrium temperature,  $T_{eq,SL}$ , turns a function of the con- 235  
187 centration of wax in oil. For example, the  $T_{eq,SL}$  is 32.0, 36.0, 236  
188 42.6, for, respectively, 5, 10, and 20 wt% of wax in oil 237  
189 (Andrade et al. 2017). All the rheometrical tests were per- 238  
190 formed in the stress-controlled rotational Malvern Kinexus 239  
191 Pro+ rheometer, equipped with serrated (0.5 mm groove 240  
192 depth) parallel plates (50 mm diameter and 1 mm gap), in 241  
193 which the temperature was controlled by a Peltier- 242  
194 thermostatic bath system. Prior to all experiments, the sample 243  
195 was loaded with the aid of a syringe on the rheometer; at this 244  
196 time, the parallel plates and the syringe were also at 60 °C in 245  
197 order to prevent precipitation of crystals during loading. 246

198 As different protocols were used, we are going to describe 247  
199 the experiments before showing each result. But it is important 248  
200 to emphasize that in all the experiments, the rate of change of 249  
201 temperature (cooling or heating rate) was kept at 1.0 °C/min 250  
202 and that all the cooling and heating processes were performed 251  
203 statically, i.e., with no shear imposed to the material. 252

## 204 Results

### 205 Material structure in the initial state

206 Let us first recall the main characteristics of the waxy oil 253  
207 suspensions in the solid regime, under fixed thermal history. 254  
208 During the cooling, the material reaches the WAT (wax 255

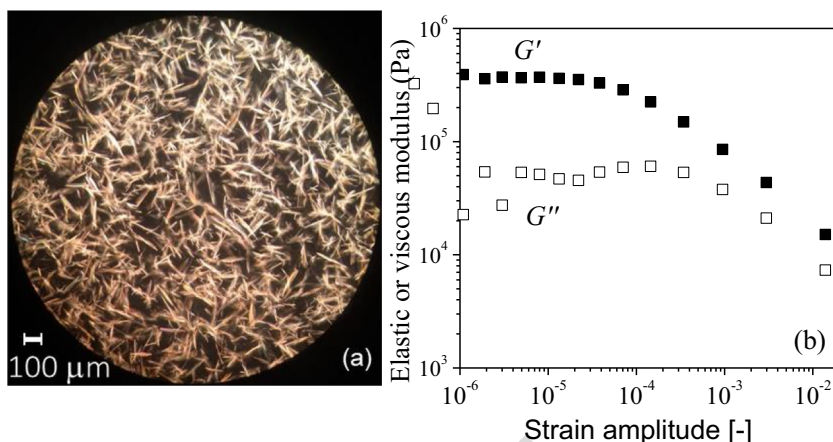
appearance temperature) and the paraffins start to precipitate 209  
as crystals structures in the material. It is known that the higher 210  
the concentration of wax in oil, the higher the WAT is 211  
(Andrade et al. 2017) and as the temperature decreases, more 212  
solid paraffins crystallize in the oil. If the cooling is performed 213  
quiescently, at a certain point, the crystals can percolate and 214  
form a structure in the material. From microscopy image ob- 215  
tained at 25 °C for 8 wt% after imposing a cooling rate of 216  
1 °C/min from 60 °C (Fig. 1), the crystals appear to present 217  
a needle-like morphology which likely forms a network of 218  
inter-particle bonds that is responsible for the initial solid- 219  
like behavior of the material. During a stress amplitude oscil- 220  
latory sweep, the material presents a very high elastic modulus 221  
( $G'$ ) in the linear regime, in the order of  $4 \cdot 10^5$  Pa (see Fig. 1), 222  
when compared to the typical values for soft-jammed systems 223  
(say, a few hundred Pascals, see Coussot et al. (2006)). The 224  
material then leaves the linear region (i.e.,  $G'$  starts to decrease 225  
with the stress imposed to the sample) at a very low strain 226  
amplitude, in the order of  $5 \cdot 10^{-5}$ , and the elastic modulus 227  
drops by several orders of magnitude. These trends suggested 228  
to consider that we are dealing with brittle soft solids. 229

230 Still under the same thermal history, it was shown that the 231  
elastic modulus in the linear regime starts to increase rapidly 232  
beyond a critical concentration of wax up to about 10 wt%. In 233  
this range, increasing the concentration just increases the num- 234  
ber of needles but does not affect the needle size (see Andrade 235  
and Coussot (2019)). The variation of the elastic modulus as a 236  
function of the concentration increment above the critical one 237  
appeared to be consistent with a percolation phenomenon in a 238  
sol-gel transition (De Gennes 1980). Around 10 wt%, the 239  
elastic modulus seems to reach a plateau (in the order of 240  
 $2 \cdot 10^6$  Pa) while the size of the needles rapidly increases, but 241  
the structure observed for concentrations beyond 10 wt% is 242  
similar to that observed at smaller concentrations with just a 243  
scale change of the elements. Besides the fact that the elastic 244  
modulus reaches a plateau, the material yield stress goes on 245  
increasing beyond the concentration of 10 wt%. The data pre- 246  
sented in Andrade and Coussot (2019) concerning the elastic 247  
modulus and the yield stress are summarized in Fig. 2. 248

249 Under a given thermal history, the solid to fluid transi- 250  
tion for such a material appears to be very abrupt. After 251  
preparation, a constant stress is imposed for some time and 252  
we follow the resulting deformation in time. At the end of 253  
this test, the material is heated again then cooled down, and 254  
a new stress value is applied. The material appears to re- 255  
main in a solid state for sufficiently small stresses, i.e., the 256  
deformation remains limited (see Fig. 3). Beyond a critical 257  
stress, the material behavior is completely different: the 258  
deformation initially slowly increases, then increases sud- 259  
denly and dramatically, giving the aspect of a vertical jump 260  
in a strain vs time diagram: the strain increases up to sev- 261  
eral orders of magnitude typically in less than one second  
(see Fig. 3). Thus, when the material reaches a critical



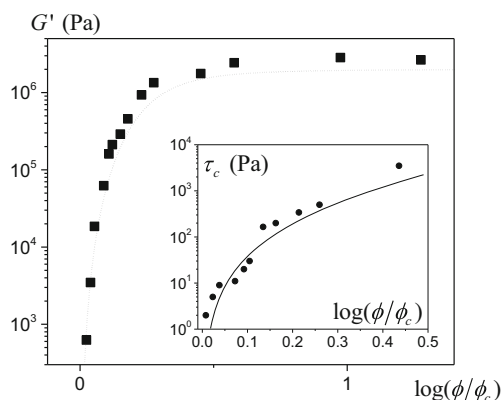
**Fig. 1** Microscopic aspect of the sample (a) and dynamic moduli as a function of the strain amplitude in an oscillatory sweep stress amplitude performed at 1 Hz (b). Image and test performed at 25 °C after the static cooling from 60 to 25 °C, with a cooling rate of 1 °C/min and a resting time of 10 min. In the image, the bright needles are the wax crystals and the black region is the oil. 8 wt% of paraffin in oil



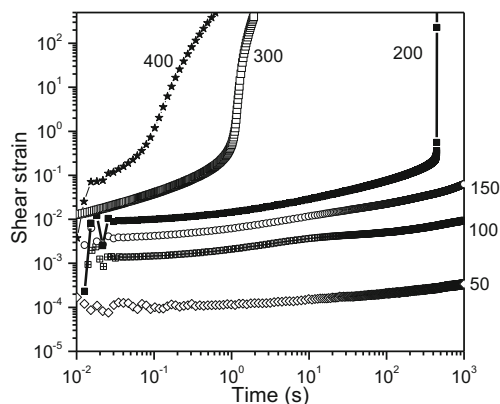
262 strain ( $\gamma_c \approx 0.1$ ), the material breaks and presents a “col-  
 263 lapse” in the sense that the shear strain evolves orders of  
 264 magnitude in a very short time. It is interesting to note that  
 265 a similar behavior was already reported by Wardhaugh and  
 266 Boger (1991) using crude oils. Then the material reaches a  
 267 liquid state, with a behavior close to a Newtonian one with  
 268 a viscosity equal to a few times that of the suspending oil  
 269 (Andrade and Coussot 2019). Note that this solid-liquid  
 270 transition appears to be irreversible over a time of obser-  
 271 vation of several days, since this liquid behavior is ob-  
 272 served to persist during such a period. In other words, it  
 273 seems that after the breakdown of the interparticle bonds,  
 274 the structure is not recoverable unless the sample is heated  
 275 to dissolve all the paraffins in the oil and cooled again to  
 276 the initial solid state. It is also worth noting that a similar  
 277 collapse may be obtained through a fatigue test, i.e., stress  
 278 oscillations of amplitude smaller than the yield stress  
 279 (Andrade and Coussot 2019). Note that a similar trend  
 280 (irreversible breakage and the fatigue process acting in  
 281 the material) was observed recently for soft solid (i.e., pro-  
 282 tein gels) (Saint-Michel et al. 2017).

**Influence of temperature on the waxy oil rheological behavior**

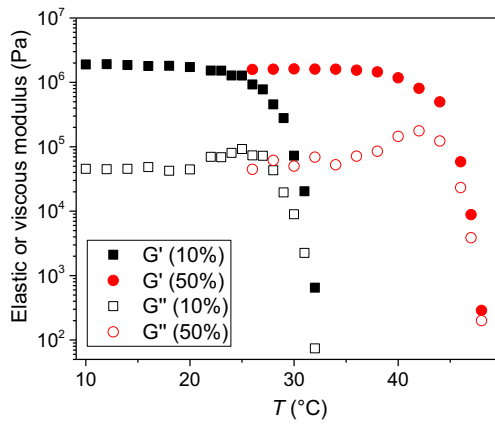
283  
 284  
 285 Let us now analyze the influence of temperature on the solid  
 286 behavior of waxy oils for different wax concentrations. All the  
 287 samples were cooled with a constant cooling rate of 1 °C/min  
 288 from 60 °C to the temperature of interest with no perturbation  
 289 in the sample and then the dynamic moduli were measured.  
 290 Due to the brittleness of the material, the dynamic moduli  
 291 were determined by imposing a stress amplitude sweep with  
 292 a trigger in the rheometer that stops the measurement when the  
 293 strain amplitude reaches  $1.10^{-5}$  in order to avoid some break-  
 294 down of the bonds in this measurement. After the oscillatory  
 295 test, the sample is cooled again to the next temperature with  
 296 the same cooling rate (1 °C/min) and rested again during  
 297 10 min before the measurement of the dynamic moduli. This  
 298 procedure was repeated for all the samples in the range of  
 299 temperature presented in Fig. 4. It is important to emphasize  
 300 that in all these measurements, the material is in thermody-  
 301 namic equilibrium, in other words, if we rest the material for  
 302 longer time at some given temperature, the dynamic modulus



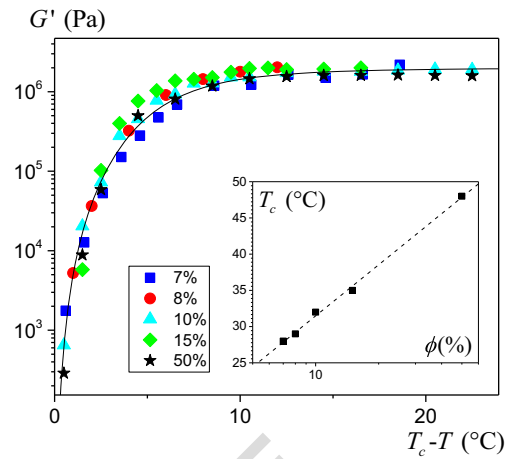
**Fig. 2** Elastic modulus (main figure) and yield stress (inset) as a function of the mass concentration of wax in oil  $\phi$ .  $\phi_c$  is the critical concentration (here equal to 5.5%) below which the value of the elastic modulus appeared negligible. Data from Andrade and Coussot (2019)



**Fig. 3** Creep test performed after the same thermal history that was imposed in the experiments performed in Fig. 1 ( $T_i = 60$  °C, cooling rate 1 °C/min and  $T_f = 25$  °C). For each test, the material is heated and cooled again in order to get the same initial state before each experiment. 8 wt% of paraffin in oil. Data from Andrade and Coussot (2019)



**Fig. 4**  $G'$  and  $G''$  as a function of temperature for 10 and 50 wt% of wax in oil



**Fig. 5** Elastic modulus for different concentrations as a function of the temperature, and critical temperature ( $T_c$ ) as a function of concentration (inset). The continuous line is Eq. (2). The dashed line in the inset is Eq. (1)

303 remains constant (see Fig. 11 in the Appendix). This means  
 304 that waxy suspensions do not present the aging process as  
 305 noticed for many yield stress materials (Joshi and Petekidis  
 306 2018) in the sense that if the waxy model oil is cooled to a  
 307 fixed temperature, the elastic modulus evolves up to a fixed  
 308 value just after the cooling and then does not evolve anymore.

309 For a given concentration, the elastic modulus starts to  
 310 increase below some critical temperature  $T_c$ , then it rapidly  
 311 tends to a plateau at a high level, i.e.  $G'_0$  (see Fig. 4).  
 312 Remarkably, the shape of  $G'(T)$  for another (for example  
 313 smaller) concentration is very similar but simply shifted  
 314 towards lower temperatures (see Fig. 4). It is also worth  
 315 emphasizing that the plateau value for the elastic modulus  
 316 does not depend on the concentration. This means that  
 317 there is a maximum elastic modulus in the linear regime  
 318 that cannot be overcome whatever the concentration. This  
 319 value appears to be close to that for the pure wax (see  
 320 Andrade and Coussot (2019)). Under these conditions,  
 321 we can rescale all the data for the different concentrations  
 322 along a master curve representing  $G'(T_c - T)$  (see Fig. 5).  
 323 Figure 5 just shows the results of  $G'$  obtained using the  
 324 same protocol as the used in the experiments of Fig. 4,  
 325 but now for five different concentrations of waxy in oil  
 326 and changing the axis to  $T_c - T$ . This allows to determine  
 327 the value of  $T_c$  [°C], which increases with the concentra-  
 328 tion,  $\phi$  [%], (see inset of Fig. 5), and whose variations may  
 329 be well represented by the following empirical equation:

$$T_c = 8 + 23.4 \times \log \phi \quad (1)$$

330

332 On the other hand, remarking that  $G' - G'_0$  varies as a power-  
 333 law when  $T_c - T$  tends to zero, with an exponent around 3, we  
 334 suggest to represent the rescaled data for the elastic modulus  
 335 in the following way (see Fig. 5):

$$1/G' = \left[ 1/G'_0 + 0.0002 \times (T_c - T)^{-3} \right] \quad (2)$$

338

339

340 On the other side, the yield stress for the different tem-  
 341 peratures may be determined from a series of creep tests  
 342 under various stress values, such as those done in Fig. 3,  
 343 for a material which has been cooled at the desired value.  
 344 However, this procedure is extremely long, since each yield  
 345 stress determination requires to impose a large set of stress  
 346 values, each time preparing again the material in the same  
 347 state according to the fixed thermal history. In order to  
 348 obtain more directly a good estimation of the yield stress,  
 349 we imposed a slowly increasing stress ramp and retained as  
 350 the yield stress the stress value for which the shear strain  
 351 exhibits an abrupt increase. This method consisting to im-  
 352 pose a slow flow is more direct on some aspects as it pro-  
 353 vides directly a “yield stress value”, whereas the creep tests  
 354 only provides a range in which lies the yield stress. On the  
 355 other side, we can fear that considering the particular brittle  
 356 behavior of these pastes, the result may be somewhat af-  
 357 fected by the procedure, but the critical stress obtained from  
 358 a series of creep tests and from such a slow stress ramp are  
 359 rather close (see Fig. 12 in the Appendix).

359 The influence of the temperature on the yield stress for  
 360 three different concentrations is presented in Fig. 6 in which  
 361 each experimental point corresponds to a sample that was  
 362 heated to the initial cooling temperature in order to dissolve  
 363 all the paraffin in oil and cooled again to the desired tem-  
 364 perature. The yield stress also starts to increase from zero  
 365 below some critical concentration (see inset of Fig. 6), obviously  
 366 similar to the critical one observed for the elastic modulus.  
 367 However, here we can observe that the yield stress does not  
 368 reach a plateau at some temperature; it goes on increasing as  
 369 the temperature decreases. As a consequence, the data for  
 370 the yield stress are not simply shifted towards lower tempera-  
 371 tures; when the concentration decreases, the yield stress  
 372 additionally increases (see inset of Fig. 6). It happens that the yield stress

369Q2

372

373 rescaled by the concentration simply falls along a master curve  
 374 as a function of the difference between the current and the  
 375 critical temperatures (see Fig. 6). The data can then well be  
 376 represented by the following equation (see Fig. 6):

$$\tau_c = 100\phi(T_c - T)^2 \quad (3)$$

378 The consistency of this representation of the data can be  
 379 checked by comparing their prediction of the variation of the  
 380 elastic modulus and yield stress as a function of the concentra-  
 381 tion with the data obtained previously (see Fig. 2). Let us  
 382 now assume that the temperature  $T_0$  is fixed. In the expres-  
 383 sions (2) and (3) the parameter is now  $T_c$ , which varies as a  
 384 function of  $\phi$  according to (1). In addition, we can define a  
 385 critical concentration  $\phi_c$  below which the material is not in a  
 386 solid state at the temperature  $T_0$ :  $\phi_c = 10^{(T_c - 8)/23.4}$ .  $T_0$ :  $\phi_c =$   
 387  $\exp(T_0 - 9)/10.1$ . From this equation and the expression (1)  
 388 we deduce

$$T_c - T_0 = 23.4 \times \log \phi / \phi_c \quad (4)$$

390 which may be inserted in (2) and (3) to obtain the expressions  
 392 of the elastic modulus and yield stress as a function of the  
 393 concentration. These expressions appear to rather well corre-  
 394 spond to the data obtained at a fixed temperature in a previous  
 395 study (see Fig. 2). It is important to emphasize that these  
 396 empirical equations are valid for the model waxy system in-  
 397 vestigated in this manuscript.

### 398 Thermal memory

399 It is well known in literature that waxy oils are thermal history  
 400 dependent in the sense that the final cooling temperature and  
 401 the cooling rate affect the rheological behavior of the material  
 402 (see "Introduction"). As far as we know, the effect of a partial

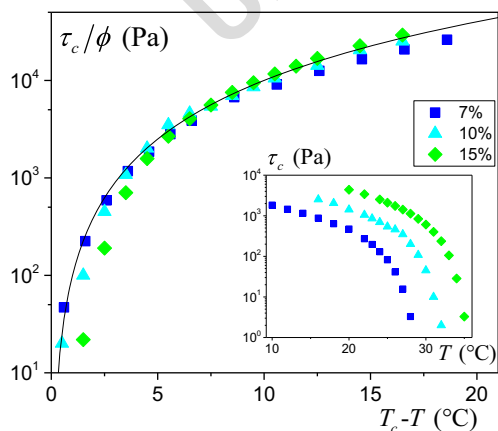


Fig. 6 Impact of temperature on yield stress. The inset shows the yield stress as a function of temperature for different concentrations. The main figure presents the same data with the yield stress rescaled by the concentration and the temperature difference with regard to the critical temperature. The continuous line is Eq. (3)

403 temperature cycle, i.e., temperature decrease then increase,  
 404 has not been studied. Let us consider a material prepared  
 405 through a given thermal history (i.e., cooling from 60 to  
 406 25 °C and resting for 10 min), and to which we impose a stress  
 407 level, with now in addition a temperature increase with a con-  
 408 stant heating rate of 1 °C/min. Looking at the strain vs tem-  
 409 perature evolution, we see that as in the case of constant tem-  
 410 perature for a stress beyond the yield stress (Fig. 3), the ma-  
 411 terial starts to flow abruptly at some critical temperature value  
 412 during the temperature increase as presented in Fig. 7. The  
 413 higher the shear stress applied, the lower is the temperature  
 414 for which this breakdown appears. The main point is that  
 415 surprisingly, the minimum temperature experienced by the  
 416 sample (in this case 25 °C) affects the yield stress of the ma-  
 417 terial: the magnitude of the stress required to break up the  
 418 structure and to start-up the flow decreases considerably when  
 419 the minimum temperature attained is decreased. For example,  
 420 the material breaks at 100 Pa when heated from 25 °C to  
 421 around 28 °C while the yield stress of this material when  
 422 cooled from high temperature to 28 °C is 201 Pa. In order to  
 423 facilitate the analysis, the inset table in Fig. 7 compares the  
 424 yield stress measured after the cooling from high temperature  
 425 to the desired temperature (values of the Fig. 6 for 10 wt%  
 426 measured at isothermal condition) and the values obtained in  
 427 Fig. 7 in which the sample experienced the minimum tempera-  
 428 ture of 25 °C (measured at non-isothermal condition, i.e.,  
 429 during the heating). We can clearly see that the critical stress  
 430 is much affected by the minimum temperature.

431 These results suggest an impact of the minimum tempera-  
 432 ture reached during the thermal history. In order to more di-  
 433 rectly observe this effect, we now follow the evolution of  $G'$   
 434 during the cooling down to a given temperature and the

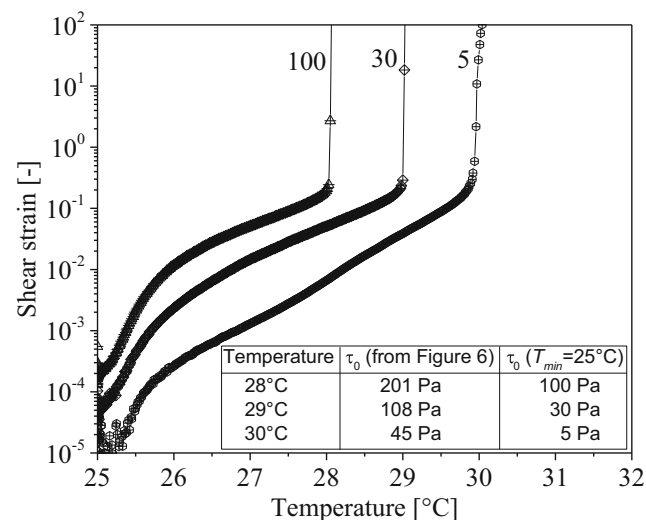


Fig. 7 Analysis of the behavior of the waxy oil during the heating. After cooling, a given stress (indicated in Pascals along the curves in the graph) is applied while the sample is heated at a constant heating rate of 1 °C/min. The values obtained from Fig. 6 were determined at isothermal conditions.  $\phi = 10$  wt%

435 subsequent heating of the material under our usual heating rate  
 436 of 1 °C/min (Fig. 8a). Note that during this process, the elastic  
 437 modulus was measured after 10 min of rest at each tempera-  
 438 ture of analysis, so that we can expect to have reached a ther-  
 439 mal equilibrium at each step of the process. Surprisingly, de-  
 440 spite this, the material strength is not only a function of the  
 441 temperature but also of the thermal history that it has experi-  
 442 enced. The  $G'$  decreases below its initial values associated  
 443 with the temperature decrease (see Fig. 8a). Moreover, the  
 444 lower the minimum temperature experienced by the sample,  
 445 the greater is the lowering of  $G'$  during the temperature in-  
 446 crease (see Fig. 8a). It nevertheless seems that decreasing the  
 447 minimum temperature to lower than 15 °C does not affect  
 448 much more the structure of the material. A similar behavior  
 449 was observed for other concentrations (see Fig. 13 in the  
 450 Appendix) and also when the experiment was performed with  
 451 a serrated surface Couette geometry (results not presented). It  
 452 is important to emphasize that without this thermal change,  
 453 i.e., if the sample is kept at the same temperature (e.g., 25 °C)  
 454 and we apply similar oscillation history, we get a constant  
 455 value of  $G'$  (see Fig. 11 in the Appendix) and not a decrease  
 456 in the elastic modulus as presented in Fig. 8.

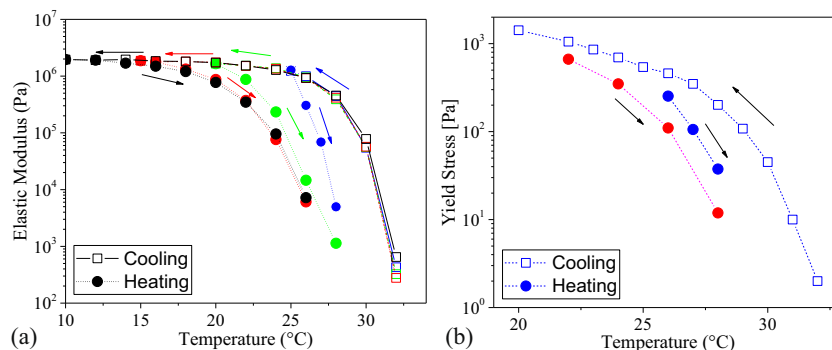
457 A similar effect is observed for the yield stress (Fig. 8b).  
 458 In this case, in these experiments we used the same proce-  
 459 dure presented in Fig. 6 but now with a thermal history in  
 460 which the sample was cooled until a minimum temperature and  
 461 heated until the temperature of test. It is important to empha-  
 462 size that for each point, after breakdown, the sample is  
 463 heated again to 60 °C in order to dissolve all the wax in  
 464 oil and the new thermal history was imposed to the materi-  
 465 al. In other words, the data presented in Fig. 8b were not  
 466 obtained successively for the same sample. We can see that  
 467 for the two minimum temperatures analyzed (25 and  
 468 20 °C), the thermal history has a great effect on the materi-  
 469 al yield stress. For example, the yield stress observed at  
 470 28 °C through our standard direct cooling procedure is  
 471 201 Pa, but drops to 12 Pa, if the material has been cooled  
 472 to 20 °C then heated back to 28 °C.

**Collapse of the structure by imposing thermal cycle**

473

474 Since the material presents a thermal memory, it seems likely  
 475 that we can weak the structure by oscillating the temperature.  
 476 In order to check that, after the standard cooling (60 to 25 °C),  
 477 we impose thermal cycles which consist to lower the temper-  
 478 ature following a linear ramp, then keeping a constant value,  
 479 and increasing again the temperature along a short linear ramp  
 480 to go back to the initial value, then again a plateau, a decrease,  
 481 and so on (see Fig. 9). It is important to mention that all the  
 482 thermal history is imposed without any stress perturbation in  
 483 the sample, and that the dynamic moduli are measured over a  
 484 relatively short time at the end of each cycle (at a temperature  
 485 of 25 °C) by imposing a stress amplitude sweep with a trigger  
 486 in the rheometer that stops the measurement when the strain  
 487 amplitude reaches  $10^{-5}$ . After each experiment, we could see  
 488 that even after the thermal cycles, the material is still in the  
 489 linear regime to strain smaller than  $10^{-5}$ .

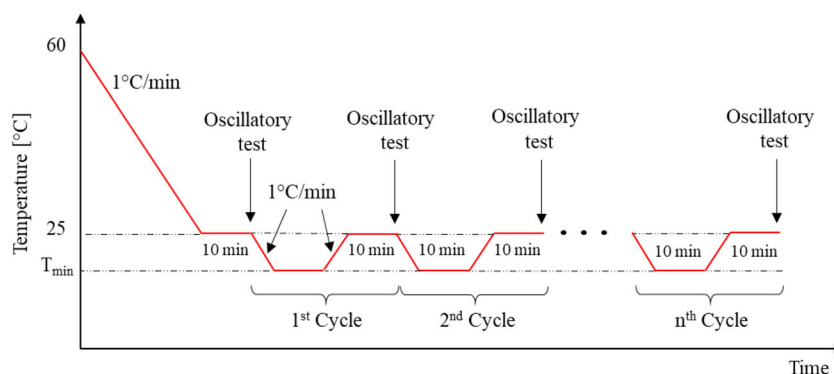
490 We can see that the dynamic moduli measured at 25 °C  
 491 decreases after imposing each cycle in the sample (Fig. 10).  
 492 This decrease is faster at the beginning then a continuous  
 493 decrease of  $G'$  is observed down to values (e.g., after the  
 494 20th cycle) which are three orders of magnitude lower than  
 495 the initial one, and of the order of those observed after the  
 496 material collapse, i.e., around  $2 \cdot 10^3$  Pa (as presented in  
 497 Andrade and Coussot (2019)). In other words, we can “col-  
 498 lapse” the structure (decreasing the  $G'$  from  $10^6$  to  $10^3$  Pa)  
 499 without imposing any stress in the sample, just by thermal  
 500 cycles. Moreover, the smaller the minimum temperature used  
 501 in these cycles the stronger the decrease of  $G'$  along the suc-  
 502 cessive cycles (see Fig. 10), so that the collapse is reached  
 503 sooner. It is important to emphasize that different protocols  
 504 were tested (not shown in order to facilitate the understanding  
 505 of the main message of the paper), and the thermal cycle also  
 506 affects the mechanical properties of the material at the mini-  
 507 mum temperature of the cycle. But in this case, the lower the  
 508 minimum temperature, the greater is the number of cycles  
 509 required to weaken the structure of the material.



**Fig. 8** a Elastic modulus as a function of temperature during the cooling and the heating phases for different minimum temperatures (from right to left)  $T_{\min} = 25$  °C (blue), 20 °C (green), 15 °C (red), and 10 °C (black)). b

Yield stress (see procedures of determination in the text) as a function temperature for two different minimum temperatures ( $T_{\min} = 25$  °C (blue) and 20 °C (red)).  $\phi = 10$  wt%





**Fig. 9** Scheme of the thermal histories used to analyze the influence of the thermal cycle on the waxy oil. The material was cooled from 60 to 25 °C, then a thermal cycle was imposed between 25 °C and  $T_{min}$

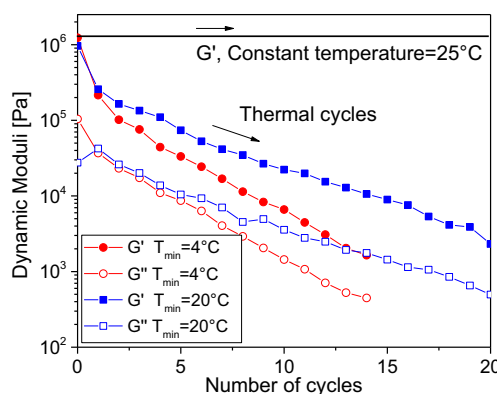
(minimum temperature). In all the temperature ramps, the rate of change of temperature is 1 °C/min regardless of whether cooling or heating is applied

510 **Discussion**

511 With our waxy oils we can see a kind of “low temperature  
 512 cracking” in which the material strength is affected by the  
 513 minimum temperature experienced by the sample (see Figs.  
 514 7 and 8) and also a thermal fatigue process, in which oscillat-  
 515 ing the temperature the material weakens and suffers a “col-  
 516 lapse” without any external stress imposed in the material  
 517 (Fig. 10). The thermal fatigue cracking is a well-known pro-  
 518 cess in metals (Starling and Branco 1997; Persson et al. 2005)  
 519 in which the materials fail when exposed to hot work thermal  
 520 cycles. In these cases, the authors state that the materials are  
 521 subjected to thermal gradients during the fast temperature  
 522 changing and, as a consequence, the thermal expansions and  
 523 contractions are not homogenous throughout the sample, gener-  
 524 ating different deformation and residual stress in the materi-  
 525 al. As a consequence, these thermal cycles can lead to fatigue  
 526 cracking at the surface of the material. It is an important issue  
 527 for die casting and warm forging industries. On the other  
 528 hand, the low-temperature cracking and the thermal fatigue  
 529 cracking at low temperatures have been studied in bitumen  
 530 to understand failure in asphalt pavements (Soenen and  
 531 Vanelstraete 2003; Kumar-Das et al. 2012). In these cases,  
 532 during the cooling, the bitumen is able to shrink and relax  
 533 the stress up to a certain temperature, but upon further cooling,  
 534 the bitumen stiffens and is no longer able to relax the stress  
 535 through a viscous mechanism. These low temperatures gener-  
 536 ate thermal cracking in the material that is also generated by  
 537 several thermal cycles.

538 In order to discuss the physical origin of this thermal fati-  
 539 gue for our waxy oils, we have to refer to their specific  
 540 structure in the solid regime (as compared to metals): this is  
 541 a rather “open” structure built on a percolated network of  
 542 needles linked by solid bonds. Moreover, the macroscopic  
 543 behavior relies on the links between the needles, as only the  
 544 links are broken during the solid-liquid transition, i.e., the  
 545 needles remain intact (see Andrade and Coussot (2019)).

This implies that what occurs inside the needles as a result 546  
 of temperature variations should play a negligible role; they 547  
 can be considered as rigid, and formed during the first thermal 548  
 cycle after preparation. Under these conditions, the impact of 549  
 temperature on the elastic modulus and yield stress is associ- 550  
 ated with the exact state of crystallization of the material com- 551  
 posing the links between needles. If the structure could simply 552  
 be considered as formed of the association of a number of 553  
 crystals increasing when the temperature decreases, decreas- 554  
 ing values of the yield stress, and the elastic modulus would be 555  
 obtained for increasing temperatures. This is indeed what we 556  
 observe. If in addition each crystal formation or fusion is ob- 557  
 tained at the same given temperature, for low temperature 558  
 variations, the thermal history cannot have any impact: the 559  
 current temperature solely imposes the structure state, hence 560  
 the mechanical strength of the material. If the temperature of 561  
 crystallization is lower than the temperature of fusion, there 562  
 might be some hysteresis, but this will only play a role during 563  
 the first thermal cycle, with little to no long-term evolution. 564



**Fig. 10** Dynamic moduli measured at 25 °C after thermal cycles (see procedure in Fig. 9). The first point (Number of cycles = 0) corresponds to the end of the cooling at rest from 60 to 25 °C and the other points correspond to the subsequent measurements after an increasing number of cycles. The upper continuous line represents the value of  $G'$  at a constant temperature, i.e., without thermal cycle.  $\phi = 10$  wt%

565 This implies that, in order to explain the thermal  
 566 fatigue of these materials, we necessarily have to con-  
 567 sider that some steps of the process alter the material  
 568 more than strictly in relation with crystallization and  
 569 fusion of some elements of the structure of the material  
 570 composing the links between the needles. In a way sim-  
 571 ilar to the thermal fatigue in metals, we can suggest that  
 572 the partial fusion of some crystals during the step of  
 573 temperature increase, alters the structure of the material  
 574 at other locations than the strict crystal under consider-  
 575 ation. This could be due to a slighter density increase  
 576 obtained after crystallization, tending to compact the  
 577 structure, while the fusion of some crystals under a  
 578 slight temperature increase would lead to a slight den-  
 579 sity decrease tending to break some “contacts” (or more  
 580 globally speaking, propagate fracture) between crystals  
 581 otherwise not altered by the thermal cycle. The succes-  
 582 sion of such cycles would then break more and more  
 583 such contacts.

584 **Conclusions**

585 The main conclusions of the work can be summarized as  
 586 follows:

- 587 • The waxy oil is a brittle material whose mechanical prop-  
 588 erties are affected by the minimum temperature experi-  
 589 enced by the material; for example, the elastic modulus  
 590 analyzed at 28 °C can decrease three orders of magnitude  
 591 and the yield stress can decrease two orders of magnitude  
 592 just by cooling statically the material to 20 °C and heating  
 593 again to 28 °C.
- 594 • Lower minimum temperatures imply a more pronounced  
 595 impact of the thermal cycle;
- 596 • If the material is thermally cycled, we can observe  
 597 thermal fatigue in the material. In other words, with-  
 598 out imposing any stress in the material, just by suc-  
 599 cessive thermal cycles, the structure “collapses” and  
 600 the material liquefies.
- 601 • This behavior could lead to important implications in the  
 602 start-up flow of waxy oils, since we show that it is possible  
 603 to decrease considerably the material yield stress just by  
 604 cycling the temperature of the material.

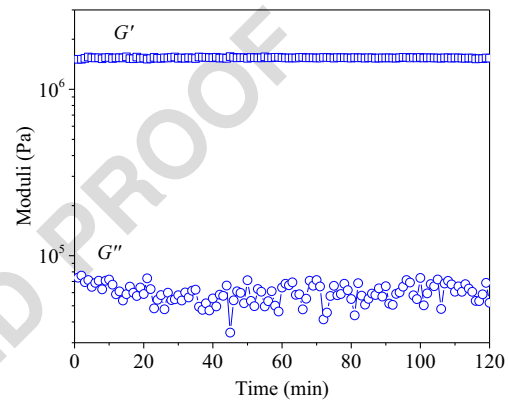
605 Understanding the exact physical origin of this behavior  
 606 would require to develop imaging technique at a very low  
 607 scale inside the wax link between needles.

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 609 the Improvement of Higher Education Personnel - Brazil) (Process:  
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**Appendix**

**Dynamic moduli as a function of time**

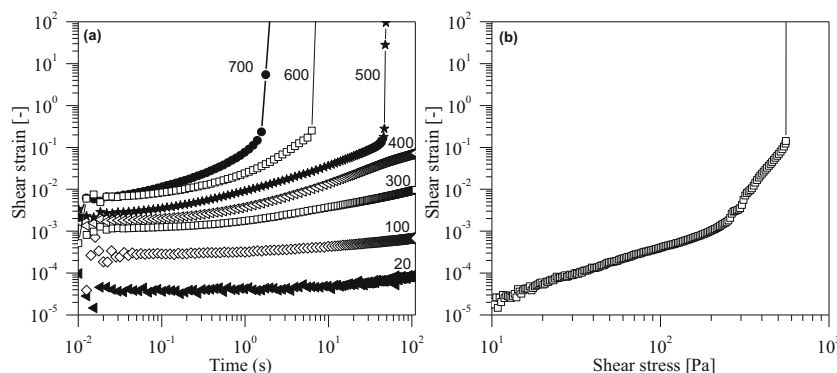
611  
 612  
 613 After the static cooling from 60 to 25 °C with 1 °C/min of  
 614 cooling rate, the material was kept at rest during 10 min and then  
 615 a constant stress amplitude oscillatory test was applied in the  
 616 material in the linear regime (stress amplitude = 10 Pa and fre-  
 617 quency = 1 Hz) and the dynamic moduli were analyzed over time  
 618 (Fig. 11). It is possible to see that in the linear regime—and if the  
 619 temperature is not changed—the strength of the material (e.g., the  
 620 elastic modulus) remains constant over time.



**Fig. 11**  $G'$  and  $G''$  as a function of time measured at a constant temperature of 25 °C after a static cooling with  $T_i = 60$  °C and cooling rate of 1 °C/min.  $\phi = 10$  wt%

**Yield stress: creep test × stress ramp**

621  
 622 As discussed in the text, the yield stress may be determined  
 623 from a series of creep tests under various stress values, as  
 624 presented for 8 wt% (Fig. 3). However, with this procedure,  
 625 a precise value of the yield stress can be obtained only after a  
 626 great number of tests. As in this work, we are analyzing the  
 627 influence of the concentration and different thermal histories  
 628 on the yield stress; determining the yield stress with a series of  
 629 creep tests would be a very slow process and almost prohibi-  
 630 tive due to the time need to get the yield stress for each con-  
 631 dition. In order to obtain more directly a good estimation of  
 632 the yield stress, we imposed a slowly increasing stress ramp  
 633 and retained as the yield stress, the stress value for which the  
 634 shear strain exhibits an abrupt increase. Just to compare, we  
 635 are showing again the results of creep test (Fig. 12a) presented  
 636 previously (Andrade and Coussot 2019) for 10 wt% of wax in  
 637 oil. In these tests, we can see that the material breaks if a stress  
 638 of 500 Pa or higher is applied in the sample. If the same  
 639 thermal history is applied in the sample but instead of a plateau  
 640 of stress, we impose a stress ramp, one can see at which stress  
 641 the material breaks analyzing the shear strain as a function of  
 642 stress (Fig. 12b). We can see that for the stress ramp, the  
 643 material was broken when the stress reached around 550 Pa.



**Fig. 12** Experiments performed with 10 wt% of wax in oil,  $T_i = 60\text{ }^\circ\text{C}$ ,  $1\text{ }^\circ\text{C/min}$  of cooling rate,  $T_f = 25\text{ }^\circ\text{C}$ , and 10 min of resting time. **a** Shear strain as a function of time in the creep test. Before each plateau of stress, the sample is heated and cooled again using the same thermal history.

(Results presented in data presented in Andrade and Coussot (2019)). **b** Shear strain as a function of shear stress in the stress ramp stress. In this measurement, the stress was increased logarithmically at a rate of one order of magnitude per each 10 min

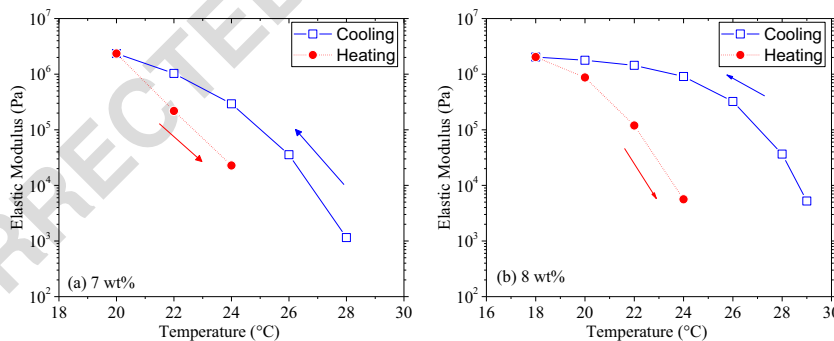
644 **Thermal memory for different concentrations**

645 The same experiment presented for 10 wt% (see Fig. 8a) was  
646 performed for two other concentrations, 7 wt% (see Fig. 13a)

and 8 wt% (see Fig. 13b). We can see that the minimum  
647 temperature also affects the strength of the material for other  
648 concentrations.

650  
651

**Fig. 13**  $G'$  as a function of temperature during the cooling (squares in blue) and for the same sample during the heating (stars in red) for **a**  $\phi = 7\text{ wt}\%$  and **b**  $\phi = 8\text{ wt}\%$



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