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**Loss of crystalline structure and swelling kinetics
of maize starch and flour granules in glycerol excess:
the role of the envelope structure**

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Abstract: Temperatures of loss of crystallinity and kinetics of swelling in glycerol excess were investigated on various maize flours and starch. The increase of amylose content in flour leads to a more persistent “crystalline” structure. This appears more clearly in differential scanning calorimetry (DSC) than in loss of birefringence, because a significant portion of the starch structure does not come only from amylopectin crystallites but also from helical arrangements. The effect of heating rate on the loss of order and on the glycerol/starch interactions was highlighted. Granule swelling tests in glycerol excess confirmed that the melting of crystallites is not a sufficient condition for complete dissolution of the granule. The granule swelling takes place in two steps for flours containing amylose, and occurs largely after gelatinization due to the importance of the granule envelope. The strength of this envelope, due to the presence of networks including proteins, lipids and amylose, is different between standard maize flour and starch. Tests in presence of lauric acid highlight the role of lipids on the granule envelope strength. The change in the viscosity of the granule/glycerol suspension during gelatinization is explained by granule swelling and can be described by a Krieger-Dougherty equation.

KEY WORDS: Maize flour, Starch, Glycerol, Swelling, Amylose, Crystallinity.

1. Introduction

Starch gelatinization has been studied for a long time (Olkku and Rha, 1978; Donovan, 1979; Ratnayake and Jackson, 2008), essentially in water, but also more recently in other liquids, like glycerol (Liu et al., 2011), NMMO (Koganti et al., 2011, 2015) and ionic liquids (Liu and Budtova, 2013; Mateyawa et al., 2013). Different methods were used to characterize gelatinization kinetics and mechanisms, like differential scanning calorimetry (DSC), optical and electron microscopy, birefringence, wide angle X-ray diffraction, light scattering, viscosity measurements. DSC is one of the most popular and was largely used to explore the phase transitions in starch/water systems (Wootton and Bamunuarachchi, 1979; Russell, 1987; Zanoni et al., 1995; Spigno et al., 2004; Sopade et al., 2004). Combinations of rheology and microscopy can also be used (Tan et al., 2008). It is reported that suspension viscosity increases during gelatinization, then reaches a peak and decreases (Eliasson, 1986; Yang and Rao, 1998; Yu et al., 2006). By studying starches of different botanical origins or with various amylose/amylopectin ratios, it was possible to evidence the strong influence of this parameter (Russell, 1987; Tester and Morrison, 1990; Cooke and Gidley, 1992; Jenkins and Donald, 1998; Fredriksson et al., 1998; Liu et al., 2006; Chen et al., 2007; Blazek and Copeland, 2008; Liu et al., 2011; Chen et al., 2011). It was shown that the amylose content is very influent on granule swelling in water excess. The granule size, the heating rate (Patel and Seetharaman, 2006) and the addition of fatty acids (Blazek and Copeland, 2009) can also change granule swelling kinetics. These fatty acids do not have the same interactions with maize starches of different amylose content (Chang et al., 2013). Some explanations of the differences in swelling kinetics regardless to the amylose content were proposed by Debet and Gidley (2006, 2007). They evidenced the role of the granule envelope structure on the swelling behaviour. This structure is due to a network made of proteins and V-type crystallites, resulting from helical arrangements of amylose chains. The recent development of plasticized starch/thermoplastic blends (St-Pierre et al., 1997; Rodriguez-Gonzalez et al., 2003; Li and Favis, 2010), based on ternary starch/glycerol/water

26 mixtures, recently led to the study of starch gelatinization in such media (Forssell et al., 1997;
27 Nashed et al., 2003; Tan et al., 2004; Li et al., 2008; Liu et al., 2011). If the gelatinization of starch
28 is well documented, it is less the case for flours. However, from an economic point of view, flour is
29 less expensive than starch to be used in blend with a thermoplastic. Consequently, it is also
30 interesting to look at flours behavior. Therefore, in the present study, we propose to characterize the
31 mechanism of starch and flour gelatinization in glycerol suspensions, and to evaluate the swelling
32 kinetics of starch and flour granules with different amylose/amylopectin contents in pure glycerol.

33 **2. Materials and methods**

34 Four starchy products, kindly provided by ULICE (Riom, France), were investigated in this study:
35 three maize flours (standard, waxy, high amylose) and a standard maize starch. SEM pictures of
36 these materials are shown in Figure 1 and their main characteristics are given in Table 1. They
37 differed either by the variety and/or the treatment, e.g. extraction of fats and proteins for the starch.
38 The three varieties of maize flour essentially differed by their respective ratio of amylose and
39 amylopectin: the waxy maize contained less than 1 wt% amylose (dry matter), whereas standard
40 maize contained about 30 wt%, and high amylose maize (or amylo maize) 70 wt%. The initial water
41 content was also different for the various starchy products: it varied from 8.4 wt% (waxy flour) to
42 12.3 wt% (standard starch). This initial water content was not modified during trials in glycerol
43 excess. Experiments at the same water content may have been of interest, but were not carried out
44 in the present study. Storage in closed bags of the samples in a freezer allowed to avoid changes in
45 water content. It was effectively checked that the storage did not modify the water content. The
46 global gelatinization process in glycerol excess is assumed to be not affected by small variations of
47 the water content. This is of course fully different from plasticization of starch at low glycerol
48 content, where small variations of the water content have an important effect on the plasticization
49 process and the product rheological behavior. The lipid content in flours was globally proportional

50 to the amylose amount. The protein content was almost zero in standard starch whereas it was quite
51 high in flours (around 9 wt%).

52 Glycerol was chosen as starchy phase plasticizer. Its melting temperature was 17°C, it is boiling at
53 290°C, but may begin to evaporate around 170°C. It had a density of 1.26 and a viscosity of 1 Pa.s
54 at 25°C.

55 Lauric acid was also used in the study. It is a mono-fatty acid, with a melting temperature around
56 45°C. It has no double bond and can create complexes with amylose.

57 Microscopic observations were performed on a Leitz microscope (Metallux 3), equipped with a
58 CCD camera (JVC KY-F75U). Observations in polarized light were made with a hot stage (Linkam
59 TMS 91) on a very dilute suspension of dry flour in glycerol, to estimate the temperature of loss of
60 crystallinity (Maltese cross extinction) and to observe the swelling of the granules with the
61 temperature.

62 Viscosity measurements under continuous shear of suspensions of granules in glycerol were carried
63 out on a parallel plate rheometer (Stresstech[®], Reologica). 40 mm diameter plates and a 1 mm gap
64 were used. The initial volume fraction of flour or starch varied between 6.3 and 6.6 wt% (2 g of
65 starch or flour suspended in 40 mL of glycerol). After a pre-shear at 25 s⁻¹ to break eventual
66 aggregates, the suspension was sheared at 16 s⁻¹, with a heating rate in the range 1 to 10°C/min.

67 Calorimetric analyzes were performed on a differential scanning calorimeter (Perkin Elmer DSC7).

68 To avoid loss of material (water evaporation), high pressure sealed capsules were used.

69 **3. Results and discussion**

70 **3.1. Gelatinization in glycerol excess**

71 We first analyzed the temperatures of loss of crystallinity in excess of glycerol. The loss of
72 crystallinity can be characterized by the loss of birefringence in optical microscopy and by the
73 appearance of a melting endotherm in DSC experiments. For the loss of birefringence, a suspension

74 of granules (flour or starch) in glycerol was observed in optical microscopy, under polarized light
75 (Fig. 2). For DSC experiments, the mixture contained 40 wt% flour (or starch) and 60 wt% glycerol.
76 Indeed, the quantity of starchy phase had to be significant in order to obtain a signal. Moreover,
77 above 50% glycerol, its amount has almost no influence on the gelatinization temperature (Van
78 Soest et al., 1996, Habeych et al., 2009). In both cases (microscopy and DSC), the heating rate was
79 10°C/min.

80 Values of temperature of loss of cristallinity, obtained by both microscopy and DSC are indicated in
81 Table 2. Values for the beginning of gelatinization are similar for all products, although high
82 amylose maize flour presents a higher melting temperature. In fact, both techniques do not detect
83 the same phenomena. Temperature range of gelatinization observed by optical microscopy
84 corresponds to the loss of birefringence due to the melting of crystallites. In comparison, melting
85 endotherms measured by DSC are due to both loss of crystallinity and dissociation of double helices
86 formed by amylose/lipid complexes (Cooke and Gidley, 1992). In addition, melting endotherms of
87 crystallites and amylose/lipid complexes (more stable) can be merged (Jenkins and Donald, 1998,
88 Matveev et al., 2001, Liu et al., 2006), explaining that the melting temperature range seen by DSC
89 is wider than the one seen by optical microscopy. The higher lipid content in high amylose flour
90 explains its broader melting endotherm (35°C) relatively to waxy maize (20°C). In addition, the
91 melting enthalpy increases with amylose content, while the degree of crystallinity is often lower for
92 high amylose starches (Tester et al., 2004). In our case, the degree of crystallinity deduced from
93 XRD experiments was 16.5 %, 21.8% and 24.8% for high amylose, standard and waxy flours,
94 respectively. This highlights the role of amylose content on a more persistent structure, mainly due
95 to more stable amylose/lipid complexes.

96 For each sample, we also observed an exotherm just before the melting endotherm (around 50°C in
97 Fig. 3). This exotherm is linked to the formation of hydrogen bonds between starch and polyols
98 such as glycerol (Van Soest et al., 1996, Smits et al., 2003, Habeych et al., 2009). This peak is only

99 observed at low water content in water/glycerol/starch mixtures. Indeed, too much water saturates
100 the hydroxyl groups of starch chains, making it impossible to link starch and glycerol (Habitante et
101 al., 2008). As for gelatinization, the transition corresponding to this peak is irreversible: nothing is
102 observed on cooling, or during a second scan (Fig. 3).

103 The location of these two peaks (endotherm and exotherm) changes when increasing the heating
104 rate from 1°C/min to 5°C/min. Fig. 4 depicts the variation of the peak temperatures with the heating
105 rate. The temperature of the endotherm peak increases slightly with the heating rate (from 113 to
106 126°C), whereas the exotherm one shows a stronger dependence (from 46 to 85°C). The melting
107 temperature of the crystals should not depend on the heating rate. The small increase of the
108 temperature of the melting endotherm with the heating rate can be interpreted as a little overheating
109 although a 10°C/min heating rate is usually chosen to avoid this phenomenon. As mentioned above,
110 the exotherm is due to another physical phenomenon. Assuming that it is linked to starch/glycerol
111 interactions, the diffusion of glycerol into starch granules must be essential in these interactions and
112 this phenomenon is thermally activated. In addition, some annealing effects on heating could not be
113 excluded. These measurements evidence a different effect of the heating rate on the two physical
114 phenomena.

115 To validate the physical interpretation for the exothermic peak, the starch suspension was left at
116 25°C for 7 days. Glycerol had thus time to diffuse into starch granules and form hydrogen bonds.
117 Accordingly, maturation of the mixture leads to the suppression of this exothermic peak (Fig. 5) and
118 the gelatinization temperature was shifted to a lower value. Smits et al. (2003) similarly reported the
119 disappearance of the exotherm on dehydrated amorphous amylopectin/glycerol mixtures after
120 storage at 20°C for 7 days.

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123

124 3.2. Microscopic observations of starch and flour swelling

125 The loss of crystallinity is a necessary but not sufficient condition to characterize the destruction of
126 the granular structure. We also measured kinetics of swelling of flour and starch granules, as the
127 swelling behavior depends on the starch structure.

128 Figure 2 shows the behavior of flour granules suspended in glycerol, with a heating rate of 5°C/min,
129 observed by optical microscopy between crossed polarizers. The Maltese cross reflects the semi-
130 crystalline structure of starch granules at low temperature. Granules start to swell just before the
131 loss of crystallinity. The gelatinization takes place over a temperature range of 10 to 20°C, at
132 around 130°C, with a gradual disappearance of the Maltese cross.

133 In the case of standard and high amylose maize flours, swelling took place in two stages: a first
134 stage where large granules (diameter $\approx 20\ \mu\text{m}$) swell just after gelatinization, and a second stage,
135 beyond 150°C, where small granules (diameter $\approx 5\ \mu\text{m}$) started to swell whereas larger ones
136 continued to swell. Waxy maize flour and standard maize starch did not exhibit this behavior.
137 Above a certain temperature, granules became less apparent: they are usually referred to as “ghosts”
138 (Fig. 2d). Thermal disturbance of the solution above 170°C make the observation of the bursting of
139 these granules unclear. Nevertheless, it occurred around 180°C and they fully disappeared at 200°C.
140 From these observations, it was possible to plot the evolution of the granule diameter as a function
141 of temperature (Fig. 6). Measurements of the diameters were carried out on a tenth of granules of
142 each type and size range, using an image analysis software. We observe an important increase of
143 diameter above 130-140°C, i.e. after gelatinization.

144 3.3. Rheological measurements during starch and flour swelling

145 Stability tests over time were carried out at room temperature and at different shear rates to ensure
146 that suspensions do not have a thixotropic behavior. Each suspension was first pre-sheared at $25\ \text{s}^{-1}$

for 60 s to disperse aggregates of granules. It was then subjected to a constant shear rate of 16 s^{-1} while temperature was increased with time from 25 to 200°C , at a constant heating rate.

The variation of the viscosity of a suspension of standard maize flour in glycerol with temperature is shown in Fig. 7. Whereas glycerol viscosity regularly decreases with temperature increase, the flour suspension shows a different behavior. Initially, the viscosity of the suspension is very close to that of glycerol, due to the low volume fraction of the dispersed phase (6.5 vol %). However, after gelatinization, the swelling, first of the granules and then of “ghosts”, results in a sharp increase in the volume fraction and therefore in the viscosity of the suspension. A two-stage process is observed in the rise in viscosity, corresponding to optical microscopy observations. The first viscosity increase should correspond to the swelling of large granules whereas the second step is attributed to the swelling of small granules. The drop in viscosity at the end of the measurement corresponds to the rupture of the “ghosts”: the suspension is then transformed into a solution.

As we can see in Fig. 7, the viscosity evolution is affected by the heating rate. The first viscosity increase, corresponding to the swelling of large granules, is clearly influenced by the heating rate. Swelling at a high heating rate begins at a higher temperature. This is in agreement with the fact that swelling of large granules occurs just after the gelatinization, whose temperature increases as the heating rate is increased (see Fig. 4). Differences of swelling kinetics with heating rate were also reported by Patel and Seetharaman (2006) in the case of water. They explained that granule swelling occurred at a higher temperature at higher heating rates, what is coherent with our observations.

The rheological behavior of all flour or starch suspensions in glycerol was later measured at the same heating rate ($5^{\circ}\text{C}/\text{min}$). Measurements for the different maize flour suspensions are compared in Fig. 7. This figure shows that the flour amylose content has a huge effect on the swelling properties of the granules. The swelling is delayed to higher temperatures and the swelling intensity (evidenced as the viscosity increase) decreases as the amylose content increases. Granules of high

172 amylose maize flour swell regularly and homogeneously. Numerous studies of starch swelling in
173 water reported similar results on the correlation between swelling properties and amylose content
174 but with a single-step swelling kinetics (Tester and Morrison, 1990; Sasaki and Matsuki, 1998;
175 Tester et al., 2000; Patel and Seetharaman, 2006; Chen et al., 2007; Blazek and Copeland, 2008).
176 The reduced swelling of enriched amylose starches was attributed to the presence of amylose/lipid
177 complexes in the granules. Debet and Gidley (2006) noticed that cleaning the surface of standard
178 maize granules allowed a more rapid swelling, but did not change the kinetics for high amylose
179 maize. They deduced that proteins and phospholipids, rather than amylose, could play a role.
180 However, other studies demonstrated that proteins and phospholipids are not sufficient to preserve
181 the integrity of starch granules without amylose (Debet and Gidley, 2006). The most probable
182 explanation is that, during lixiviation, proteins present on the granule surface limit the diffusion of
183 amylose chains. These amylose chains may complex and form a network with the phospholipids on
184 the granule surface. Granule swelling would thus result from a competition between starch/glycerol
185 interactions, leading to swelling, and the strength of the network created at the surface by proteins
186 and amylose/lipid complexes. The fact that small granules present a reduced swelling after
187 gelatinization compared to large ones could be related to the surface/volume ratio, which is more
188 important for small granules.

189 The behaviors of standard maize flour and starch are depicted in Fig. 9. Contrarily to flour, starch
190 swelling is very fast and occurs in one single step. As it contains very few proteins and lipids, the
191 surface network cannot be built. Consequently, the behavior of flour and starch should be different
192 in terms of transformation and processing, at least in processes with a large amount of plasticizer. In
193 plasticized starch and in plasticized starch/thermoplastic blends, where the amount of glycerol is
194 typically 33-36 wt% (St-Pierre et al., 1997; Li and Huneault, 2011), it would be interesting to see if
195 the difference in the envelope strength can still be detected in compounding conditions. We recently
196 showed that the rheological behavior and the morphology of plasticized flour/thermoplastic blends

197 were determined by the amylose/amylopectin ratio, the plasticizer content and the processing
198 conditions, as for plasticized starch/thermoplastic blends (Deme et al., 2014).

199 Becker et al. (2001) studied the influence of a thermal treatment with glycerol stearate on various
200 starches. They showed that enriched amylose starches exhibited a reduced swelling in water,
201 contrarily to waxy maize starch which swelled even in cold water. In the present case, we
202 investigated the effect of adding 0.2 g of lauric acid (corresponding to 10 wt% relatively to starch
203 phase) in the standard maize starch suspension. Lauric acid is a fatty acid without insaturation, able
204 to easily complex with amylose (Tang and Copeland, 2006). We can see in Fig. 10 that the addition
205 of lauric acid results in a two-step swelling for the standard maize starch granules, like for flour
206 granules. Swelling is thus delayed in presence of fatty acid, confirming the crucial role of the
207 formation of amylose/lipid complexes at the granule surface. As expected, in the case of waxy
208 maize flour, the effect of lauric acid is insignificant on the granule swelling (represented by the
209 viscosity increase), as shown in Fig. 11.

210 Measuring swelling kinetics of the granules by optical microscopy (Fig. 6) allows us to establish a
211 relationship between the evolution of the suspension viscosity and the one of the granule volume
212 fraction ϕ . The evolution of the volume fraction ϕ can be deduced from the evolution of the granule
213 diameter. By introducing this volume fraction into a rheological law of suspension, it is possible to
214 calculate the viscosity evolution with temperature. This calculation of the suspension viscosity from
215 the knowledge of the granule size was performed although experimental conditions in which
216 rheological and optical measurements were conducted were very different. In optical
217 microscopy, the granule swelling was followed at rest and in a very dilute suspension. In
218 rheometry, the granule swelling was followed under shear in a more concentrated medium (6.5
219 vol%). Anyway, we tried to evaluate the viscosity evolution by using a Krieger-Dougherty equation
220 (Krieger and Dougherty, 1959):

$$\eta(T) = \eta_0(T) \left(1 - \frac{\phi(T)}{\phi_{max}} \right)^{-a} \quad (1)$$

where $\eta_0(T)$ is the viscosity of the glycerol, ϕ_{max} is the maximum packing volume fraction and a is an exponent, function of the maximum packing fraction and of the intrinsic viscosity of the solid filler. ϕ_{max} and a values depend on type, shape and size polydispersity of the particles. For example, $\phi_{max} = 0.74$ and $\phi_{max} = 0.64$ are classical values for a suspension of rigid monodispersed spheres in face centered cubic and random class packing, respectively. a is often equal (or close) to 2 (see for example Quemada, 2006). Fig. 12 shows that, for the standard maize flour, the model provides a correct approximation of the viscosity change, despite a slight overestimation at low temperatures. This prediction was obtained for $\phi_{max} = 0.52$ and $a = 3$.

Similar calculations were performed for the other varieties of granules. The values of ϕ_{max} and a determined for the standard maize flour suspensions were used for the viscosity estimation of the other suspensions. Fig. 13 shows the comparison between experimental measurements and the evolution of the viscosity using the Krieger-Dougherty law. In each case, for the different varieties of flours and starch, the evolution of the solid volume fraction with temperature was calculated from the experimental measurements of the granule diameter kinetics. We can see that there is quite a good agreement between experimental measurements during the swelling step and the Krieger-Dougherty prediction. This confirms that the viscosity evolution is essentially related to the granule swelling and corresponding change in volume fraction.

4. Conclusion.

We investigated the loss of crystalline structure and swelling kinetics of various maize flours and starch in excess of glycerol. Loss of crystallinity was investigated by DSC and optical microscopy. Swelling kinetics was followed by optical microscopy and via viscosity measurements.

243 The present work allowed us to highlight differences in temperature of loss of crystallinity for
244 different varieties of flours in excess of glycerol. It appears that an increased amylose content
245 makes the flours more difficult to gelatinize. This is more clearly seen in DSC measurements than
246 by observations of loss of birefringence, because a significant portion of the starch structure comes
247 not only from amylopectin crystallites but also from helical arrangements linked to amylose/lipid
248 complexes. A different effect of the heating rate on the ordered structure and on interactions
249 between glycerol and starch was evidenced.

250 We observed the same differences in swelling, because the swelling starts after gelatinization
251 occurs. Granule swelling in water depends on the amylose content, but occurs in one step. In excess
252 of glycerol, a two-step process is observed for flours containing amylose, which confirms that the
253 ghost integrity is kept by the envelope strength.

254 Swelling mechanisms in glycerol are the same as those observed in water, but the envelope
255 structure is more persistent. The strength of this envelope also comes from the formation of
256 networks including proteins, lipids and amylose. This explains the greater difficulty to deconstruct
257 granules of standard maize flour than standard maize starch, which contains much less fat and
258 protein than the flour. When processed at high level of plasticizer, flour (containing amylose)
259 should be thus more difficult to destructure than starch. Tests in presence of lauric acid highlighted
260 the role of lipids on the envelope strength.

261 These results can explain the existence of persistent “ghosts” in glycerol/flour mixtures, even at
262 high temperature, without intensive shear or addition of water.

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268 temperatures.

269

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383

Figure captions

Fig. 1. SEM micrographies of the pristine granules. (a) standard maize flour, (b) waxy maize flour, (c) high amylose maize flour, (d) standard maize starch. The white spots on the flour pictures correspond to minerals (calcium, magnesium, phosphorus) (0.5 to 1.3 wt% on dry basis)

Fig. 2. Optical observation of the swelling of granules of flour suspended in glycerol versus temperature: (a) to (c) between crossed polarizers, (d) to (f) without polarizers, heating rate of 5°C/min.

Fig. 3. DSC thermograms (endo up) of a glycerol/maize starch suspension during first and second heating at 5°C/min. Thermograms were vertically shifted for sake of clarity.

Fig. 4. Variation of temperatures corresponding to endothermal and exothermal peaks with the heating rate of a glycerol/maize starch suspension.

Fig. 5. Effect of the maturation time on the exothermal peak of a glycerol/maize starch suspension (5°C/min). Thermograms were vertically shifted for more clarity.

Fig. 6. Evolution of the granule diameter with temperature for a standard maize flour in glycerol at 10°C/min: case of small and large granules.

Fig. 7. Effect of heating rate on the viscosity evolution with temperature of a standard maize flour suspension in glycerol: ●: 1°C/min, △: 5°C/min, ○: 10°C/min.

Fig. 8. Effect of amylose content on the viscosity evolution with temperature (10°C/min) of maize flour suspensions in glycerol: ●: standard maize, ○: waxy maize, △: high amylose maize.

Fig. 9. Evolution of the viscosity with temperature (10°C/min) of standard maize flour (●) and starch (○) suspensions in glycerol.

408 Fig. 10. Influence of lauric acid on the viscosity evolution with temperature (10°C/min) of standard
409 maize starch in glycerol excess (●: starch, ○: starch with lauric acid).

410 Fig. 11. Influence of lauric acid on the viscosity evolution with temperature (10°C/min) of waxy
411 maize flour in glycerol excess (●: waxy maize flour, ○: waxy maize flour with lauric acid).

412 Fig. 12. Viscosity evolution with temperature (10°C/min) of standard maize flour suspension in
413 glycerol. Comparison between experiment (○) and model (—).

414 Fig. 13. Viscosity evolution with temperature (10°C/min) of flour and starch suspensions in
415 glycerol. Comparison between experiment (symbols) and model (lines). ○, — : waxy maize
416 flour, □, — : high amylose maize flour, ●, : standard maize starch.

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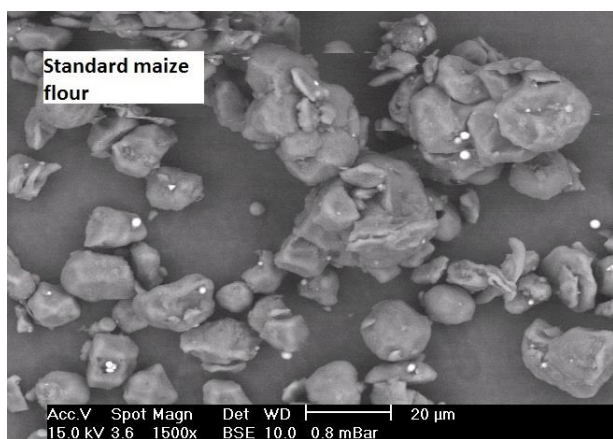
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	Standard maize starch	Standard maize flour	Waxy maize flour	High amylose maize flour
Raw density (g/L)	1470	1407	1449	1420
Amylose (wt%)	30	30	1	70
Water (wt%)	12.27	8.76	8.39	9.44
Proteins (wt%)	0.4	8.33	9.16	9.8
Lipids (wt%)	0.92	2.9	1.66	5.49
Ashes at 900°C (wt%)	0.06	0.9	0.53	1.29

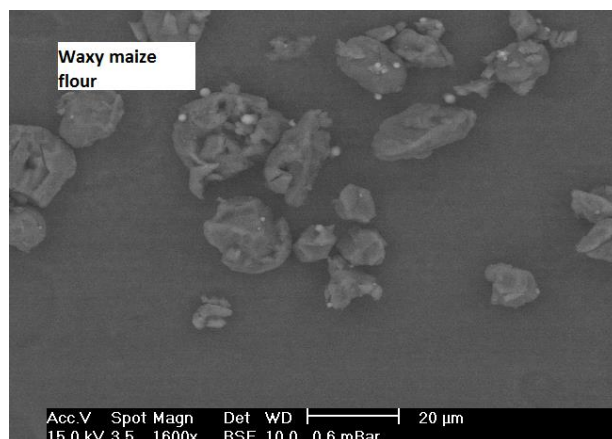
Table 1. Starchy products density and composition (in weight % of dry matter).
Data provided by ULICE

	Microscopy			DSC			Enthalpy (J/g)
	T_{onset} (°C)	T_{end} (°C)	T_{average} (°C)	T_{onset} (°C)	T_{end} (°C)	T_{average} (°C)	
Standard maize starch	129	143	136	100	140	121	4,1
Standard maize flour	128	137	132	113	159	127	4,9
Waxy maize flour	123	133	128	110	148	130	2,4
High amylose maize flour	130	150	140	110	175	145	6,0

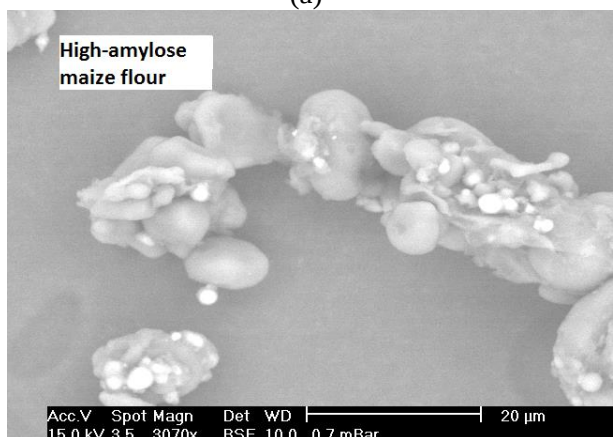
Table 2. Temperatures of loss of birefringence (microscopy) and gelatinization (DSC) of starch and flour granules in glycerol excess.



(a)



(b)



(c)



(d)

Fig. 1. Demé et al.

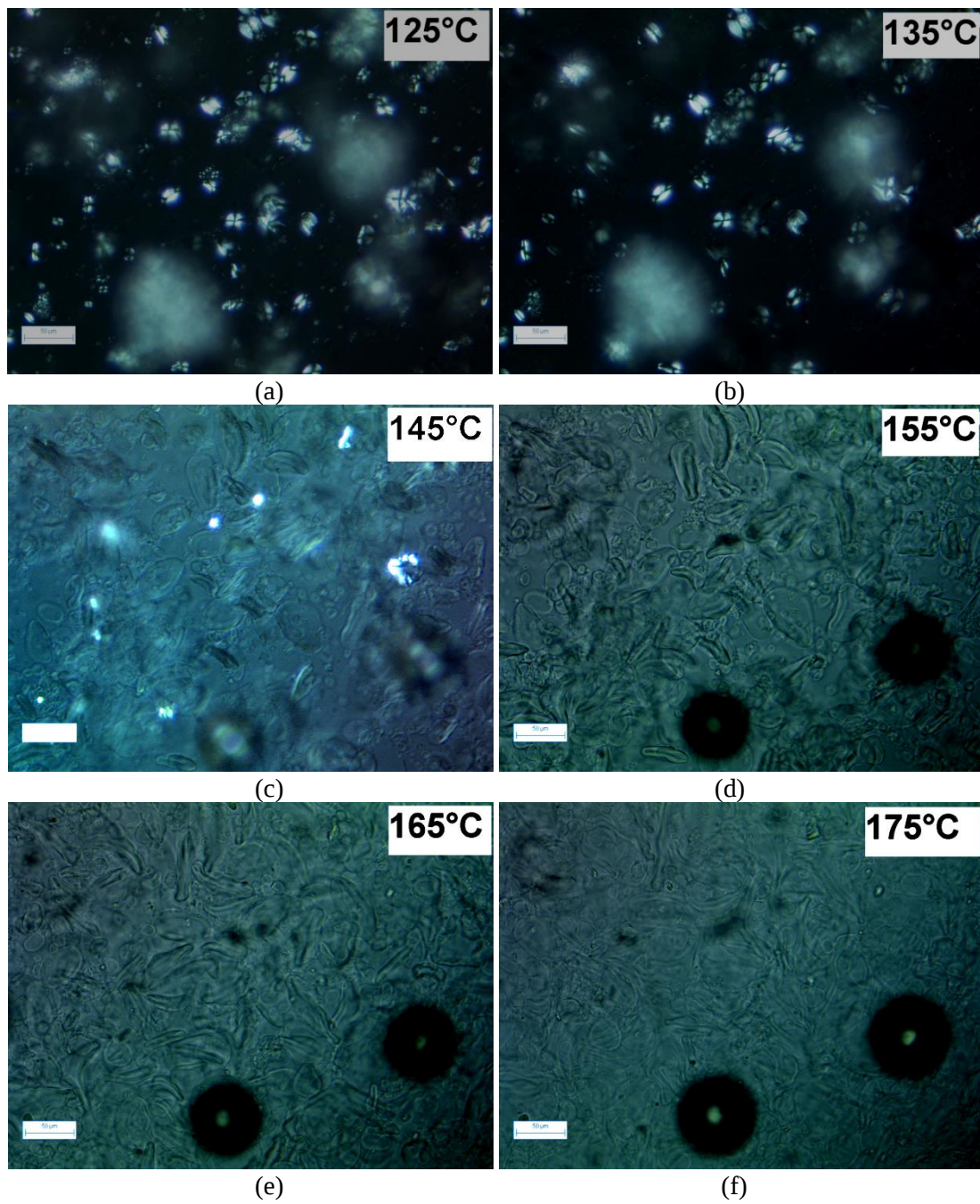


Fig. 2. Demé et al.

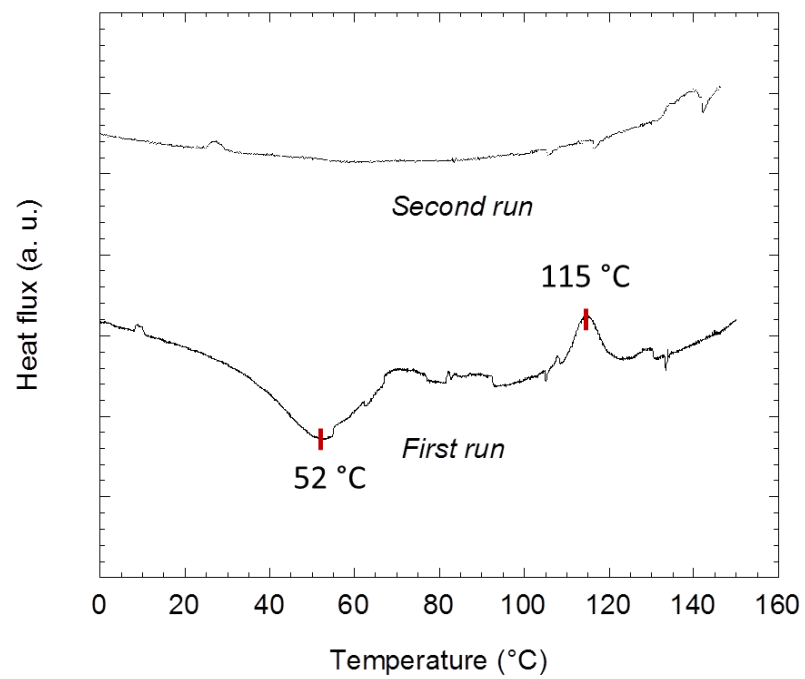


Fig. 3. Demé et al.

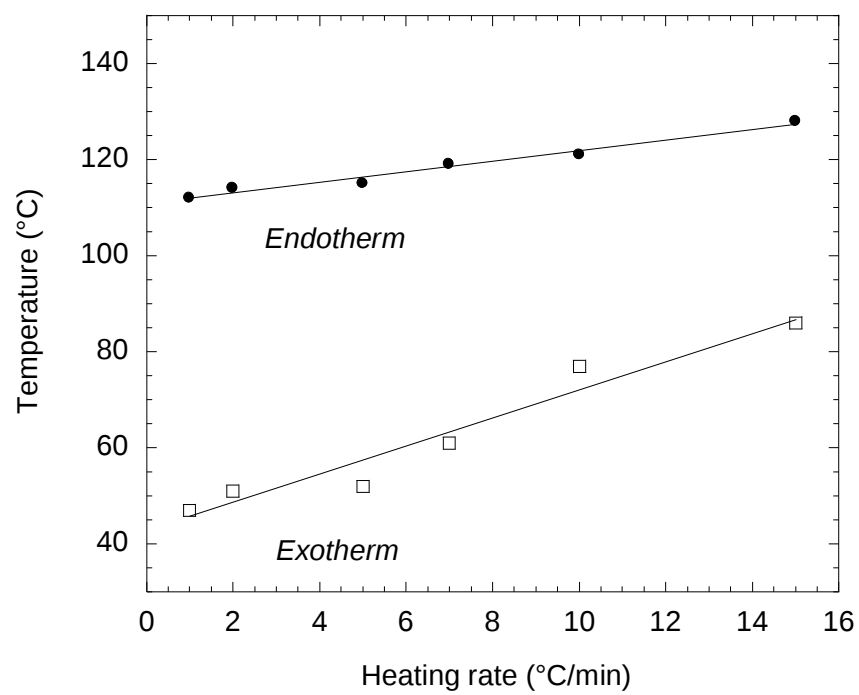


Fig. 4. Demé et al.

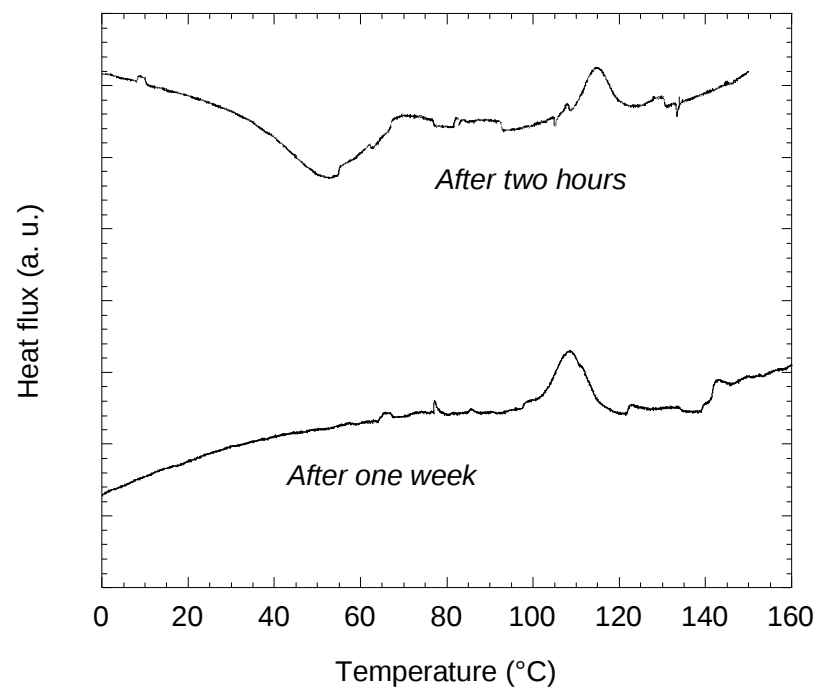


Fig. 5. Demé et al.

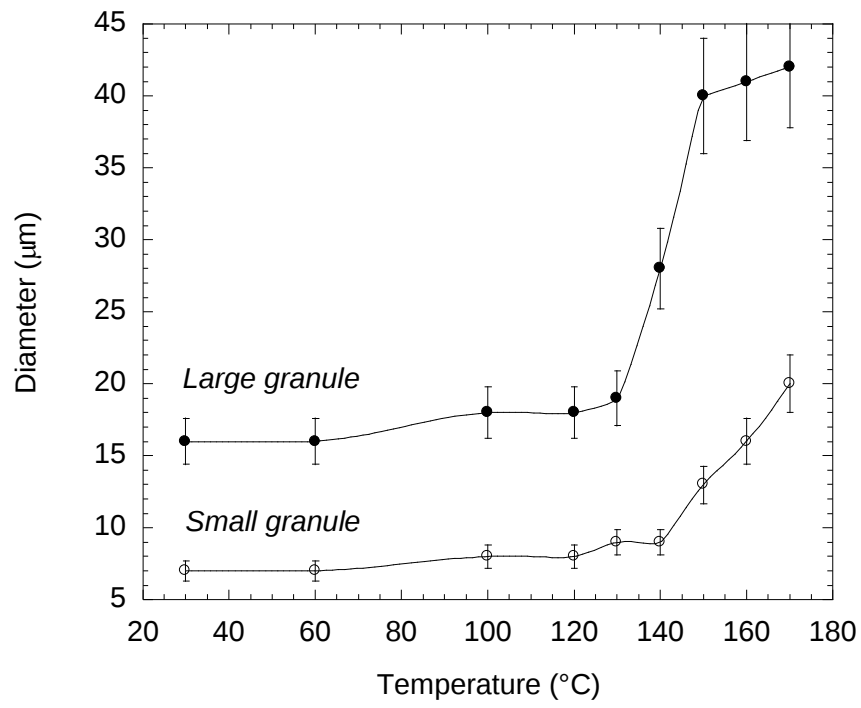


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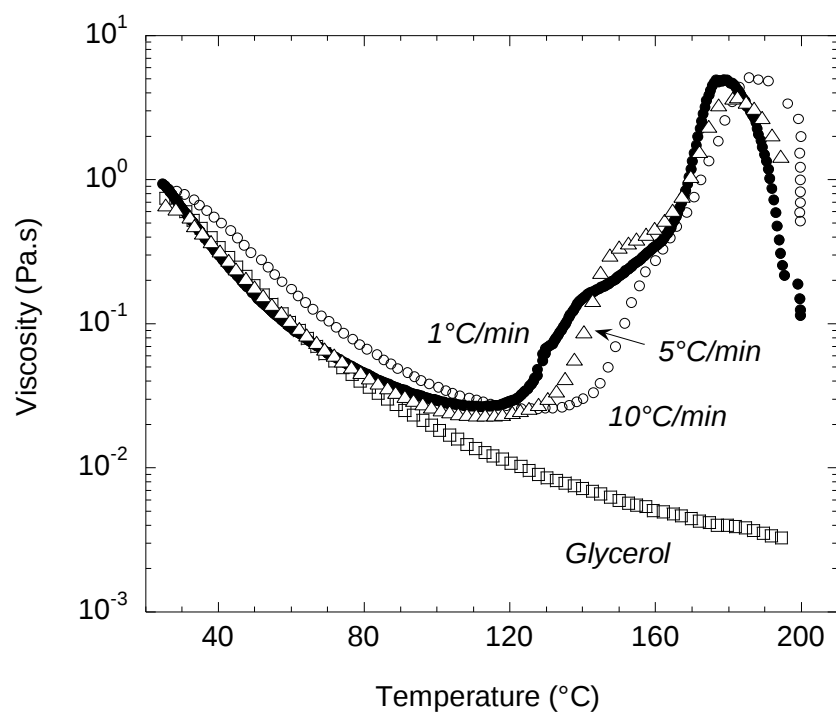


Fig. 7. Demé et al.

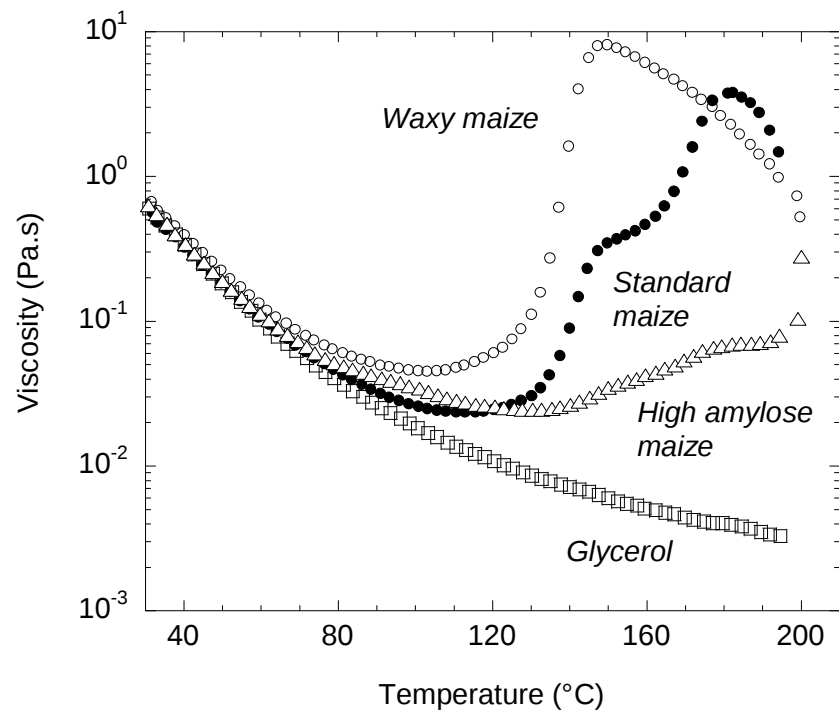


Fig. 8. Demé et al.

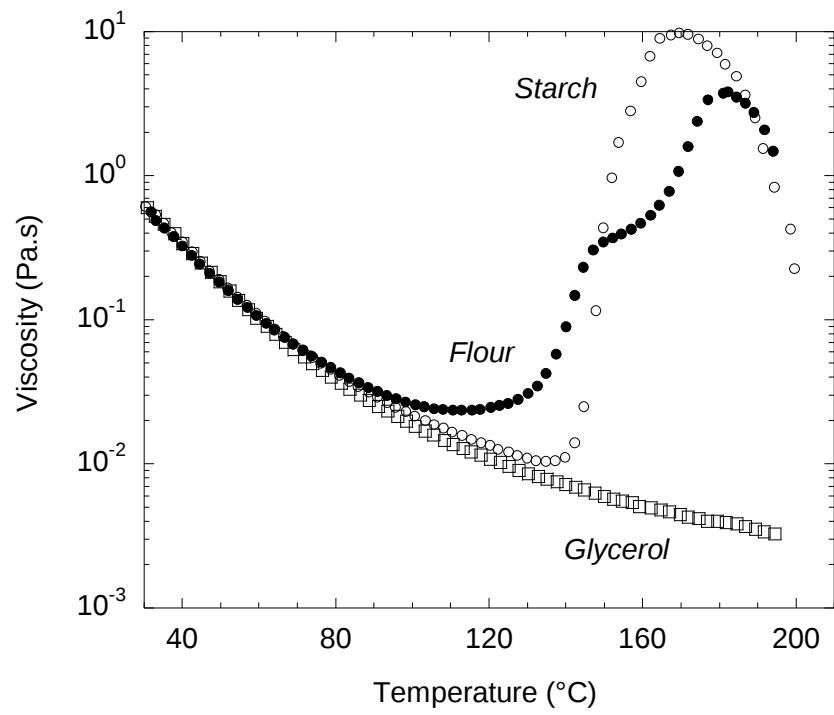


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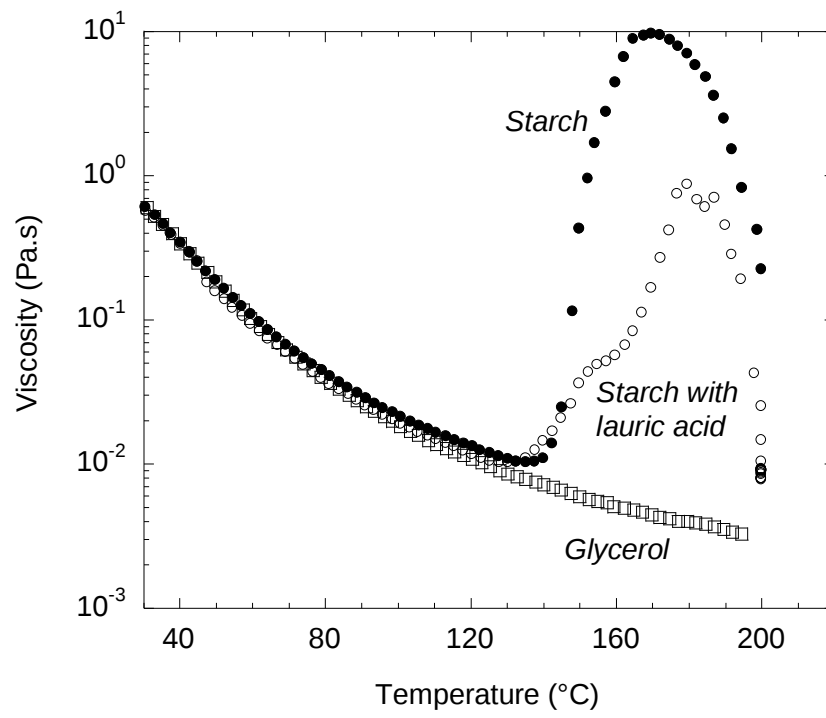


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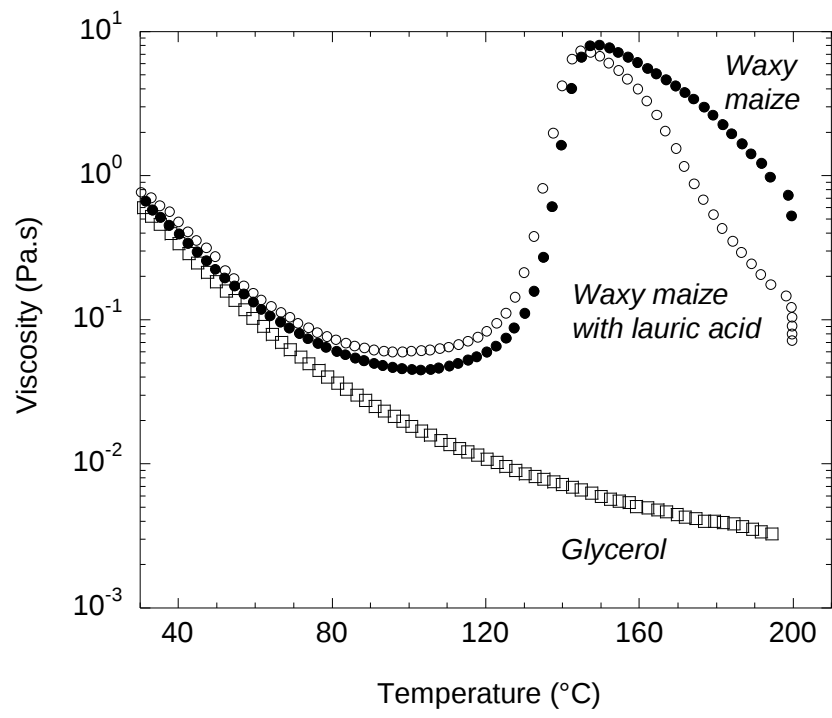


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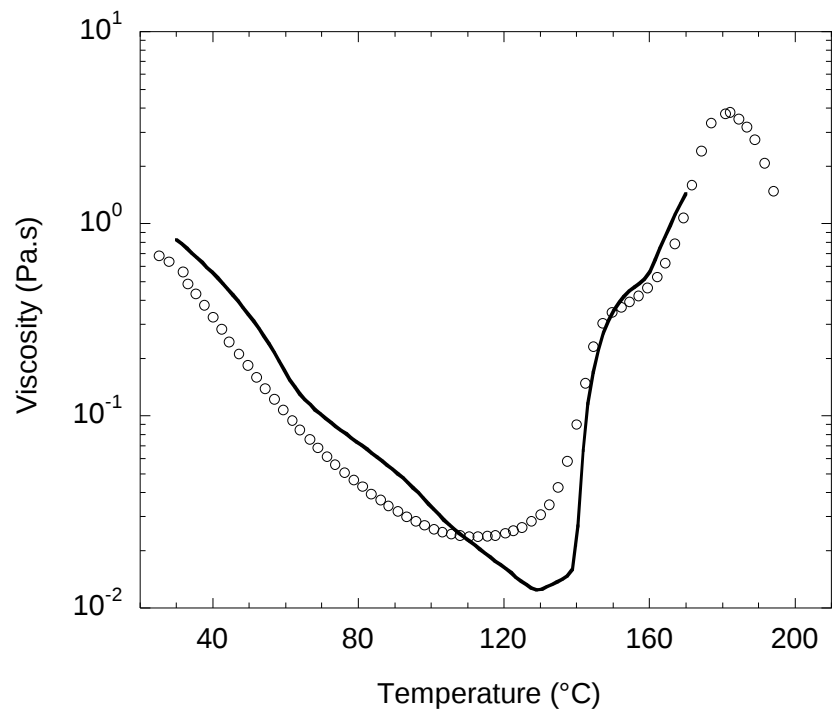


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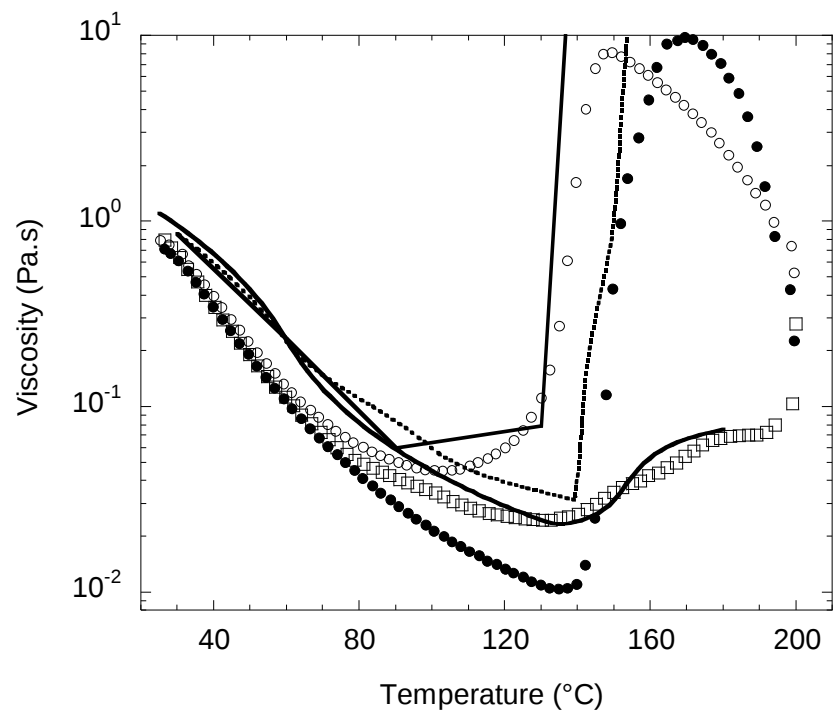


Fig. 13. Demé et al.