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1 **The viscoelastic behaviour of raw and anaerobic digested sludge: strong similarities with**
2 **soft-glassy materials**

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12
13
14 Abstract

15
16 Over the last few decades, municipal and industrial wastewater treatment activities have been
17 confronted with a dramatically increasing flow of sewage sludge. To improve treatment efficiency,
18 process and material parameters are needed but engineers are dealing with vast quantities of
19 fundamentally poorly understood and unpredictable material. Thus, accurate prediction of critically
20 important, but analytically elusive process parameters is unattainable and is a matter of grave
21 concern. Because engineers need reliable flow properties to simulate the process, this work is an
22 attempt to approach sludge rheological behaviour with well-known materials which have similar
23 characteristics. Sludge liquid-like behaviour is already well documented so, we have focused
24 mainly on the solid-like behaviour of both raw and digested sludge by performing oscillatory
25 measurements in the linear and non-linear regimes. We have shown that the viscoelastic
26 behaviour of sludge presents strong similarities with soft-glassy materials but differences can be
27 observed between raw and digested sludge. Finally, we confirm that colloidal glasses and
28 emulsions may be used to model the rheological behaviour of raw and anaerobic digested sludge.

29
30
31 Keywords

32
33 Glassy materials, rheology, sewage sludge, soft matter, time-temperature superposition, visco-
34 elasticity

37 Introduction

38

39 Sewage sludge production is the residue of wastewater treatment and by definition can't be
40 avoided. In the EU it is produced at more than 30 000 tonnes (dry matter) per day and will increase
41 by at least 10 % in 2020 (EUREAU, 2012). These volumes have to be treated and reused.

42 Slatter (1997, 2001, 2003, 2004 and 2008) has consistently shown that sludge rheology plays a
43 fundamentally important role in analysing the hydrodynamic behaviour of the sludge, as it flows in
44 pipes or in tanks and reactors, such as anaerobic digesters. However, sludge properties
45 continuously evolve due to the ongoing biochemical reactions, and for this reason it cannot be
46 used as a reference material for the design of industrial processes: engineers need reliable and
47 repeatable flow properties to simulate the process. Thus, various researchers attempted to use
48 model fluids instead of sludge, such as kaolin suspension for the yield stress determination
49 (Spinosa and Lotito, 2003), polymeric gels (Legrand et al., 1997), polyvinyl chloride (PVC)
50 suspensions (Bongiovanni, 1998), polystyrene latex (Sanin and Vesilind, 1996), but none of these
51 was particularly successful because each of these model fluids was only representative of a
52 particular application. To model the flow properties of sludge, mainly in its liquid regime, kaolin
53 suspensions are often used (Heritier et al., 2010) because it shows shear-thinning behaviour with a
54 yield stress, modelled with a Herschel-Bulkley model (Masalova et al., 2006). Even if this model
55 fluid can be used to simulate high velocity flows, it is not suitable for simulating the liquid-like
56 behaviour at intermediate shear rates, nor the solid-like behaviour at low shear rates, which
57 appears to be crucial in order to avoid – or at least minimize – dead zones in reactors, such as
58 anaerobic digesters or aeration basins.

59 Because of its fundamental nature, sludge is a very complex mixture of unknown composition and
60 its rheological behaviour is highly dependent of the treatment processes: accurate prediction of
61 critically important, but analytically elusive, process parameters is unattainable and is a matter of
62 grave concern.

63 For sake of simplicity, in the following we will only distinguish between raw, activated and
64 anaerobically digested sludge, respectively representative of the outlet of sludge treatment when
65 no tertiary treatment is applied and when anaerobic digestion is implemented. Both are
66 temperature-dependent (Dieude-Fauvel et al., 2009; Baudez and Slatter, 2012), present
67 viscoelastic properties at low shear stress and a shear-thinning behaviour at high shear stress

68 (Baudez and Coussot, 2001, Baudez et al., 2011), but at intermediate shear stresses, raw sludge
69 is a thixotropic material (Tabuteau et al., 2006, Baudez, 2008) with ageing effects (Baudez, 2008)
70 while anaerobic digested sludge highlights shear banding (Baudez et al., 2011).

71 Raw and digested sludge are mainly composed of water (more than 95%) and the remaining part
72 is made of organic matter and bacteria which tend to aggregate forming flocs. That is the usual
73 'chemical' definition of sludge: organic flocs suspended in water. However, physically, sludge can
74 also be visualised as interacting particles in a suspending medium: bacteria form extra polymeric
75 substances (EPS), finally presenting a three-dimensional gel-like biofilm matrix (Wingender et al.,
76 1999). EPS are highly charged polymers that interact with water in a manner similar to gels
77 (Keiding et al., 2001, Sutherland, 2001). They interact with divalent metal ions to form sludge flocs
78 in both aerobic and anaerobic treatment systems (Higgins and Novak, 1997). Flocs in activated
79 sludge usually carry negative charge at neutral pH. It has been found that the extracellular
80 polymeric substances (EPS) contribute to the negative surface charge of the sludge flocs (Jia et
81 al., 1996; Liao et al., 2001). As regards the influence of the anaerobic digestion, Jia et al. (1996)
82 also observed that during batch tests both surface charge and EPS content change significantly.

83 Polysaccharides and proteins were found to be the most significant surface polymers in activated
84 (raw) sludge (Forster, 1983), and the two types of binding mechanisms between water molecules
85 and the EPS structure are considered to be electrostatic and hydrogen bonds (Flemming, 1996).

86 Digestion leads to the transfer of bigger flocs into smaller ones (Mahmoud et al., 2006) and
87 disintegration of the organics brings the solids to a homogeneous grain structure, with an increase
88 of the quantity of colloidal particles (Turovskii and Matai, 2006) and a decrease of EPS
89 (Karapangiotis et al., 1998). The anaerobic digestion data showed strong correlations between
90 soluble protein generation and ammonium production (Park et al., 2006). The most important
91 constituents in digested sludge are proteins and lipopolysaccharides (Forster, 1983), which are
92 amphiphile lipids with both hydrophilic and hydrophobic heads. Novak et al. (2003) found the
93 protein concentration was 3–5 times greater than the polysaccharide concentration in anaerobic
94 systems compared to aerobic ones. They also noticed an increase of monovalent cations.

95 From a physical point of view, anaerobic digested sludge appears to be a stable suspension with
96 low settling ability (Namer and Ganczarczyk, 1993) and low surface charge (Forster, 2002)
97 indicating that interactions are more steric than electrostatic.

98 Moreover, Mikkelsen and Keiding (2002) showed that the ratio between protein and
99 polysaccharides are more or less of the same order between activated and (mesophilic) digested
100 sludge, but the degree of dispersion is 20 times higher after anaerobic digestion, indicating that
101 sludge structure is strongly affected by anaerobic digestion.

102

103 In this paper, we intend to draw parallels between well-known materials and sludge. These well-
104 known materials could then be used a model fluids to emulate the rheological behaviour of sludge
105 for the investigation and design of treatment technologies. Because the liquid-like behaviour of
106 sludge is well documented, we will intentionally focus on the solid-like behaviour of both raw and
107 digested sludge by performing oscillatory measurements in the linear and non-linear viscoelastic
108 regimes. We show that the viscoelastic behaviour of sludge presents strong similarities with soft-
109 glassy materials but differences can be observed between raw and digested sludge. Stress and
110 frequency sweeps were conducted at different temperatures to demonstrate that Brownian motion
111 also plays a role in the build-up and break-down of sludge structure. Finally, we demonstrate that
112 colloidal glasses and emulsions may be used to model the rheological behaviour of raw and
113 anaerobic digested sludge.

114

115 Materials and methodology

116

117 Sludge was obtained from the Mount Martha wastewater treatment plant (Melbourne, Victoria,
118 Australia) at the inlet (called raw sludge in the following) and the outlet (called digested sludge) of
119 the digester number 1. The initial concentration of the raw sludge was found to be 45g.L^{-1} (this
120 relatively high concentration was obtained after flotation thickening, without chemical conditioning)
121 while the solid concentration of the digested sludge was found to be 18.5g.L^{-1} . The latter was also
122 gently concentrated to 32g.L^{-1} (and 42g.L^{-1} after a second sampling for time sweep experiments)
123 by using a Buchner vacuum. These concentrations were chosen to be representative of thickened
124 sludge which is more often used in digesters. Digested samples were stored at 4°C for 30 days
125 before experiments were conducted to ensure no temporal variability, allowing us to use the same
126 material for several days of testing. This technique was successfully used by Curvers et al. (2009).

127 On the other hand, because of their high degree of fermentation, raw sludge was stored only 5
128 days before experiments. Although storage implied changes in the composition of the raw sludge,
129 considering the duration of rheological characterisation, especially the frequency sweep, we
130 needed to consider raw sludge as a 'stable' material, from both the biological and chemical points
131 of view during our whole investigation. Because changes are very fast the 72 first hours (Baudez
132 and Coussot, 2001), 5 days appears to be the shortest duration that we could manage with in order
133 to ensure that we dealt with the same material in a short window of 24 hours.

134

135 Time, stress and frequency sweep measurements were carried out with a stress-controlled
136 DSR200 instrument from Rheometric Scientific, connected to a temperature controlled water bath.
137 The rheometer was equipped with a cup and bob geometry (inner diameter: 29mm, outer diameter:
138 32mm, length: 44mm). Temperature varied from 10 to 80°C (high temperatures were applied to
139 highlight thermal phenomena).

140 To avoid evaporation, sludge was covered with a thin film of known viscosity Newtonian oil: oil and
141 sludge are not miscible, as evidenced by oil removal processes in wastewater treatment plants.

142 Before each measurement, sludge was strongly pre-sheared at a shear rate of 500s^{-1} for 5 minutes
143 and then left at rest respectively for 2 minutes for time sweeps, 5 minutes for strain sweeps and 1
144 hour for frequency sweeps. This procedure allowed us to obtain reproducible results (Baudez et
145 al., 2011).

146

147 Results and discussion

148

149 Time sweep

150 Under constant stress, low enough to be in the linear viscoelastic regime (Ayol et al., 2006) and
151 constant frequency, raw sludge aged with a monotonic decrease of the shear strain while the
152 digested sludge reached an equilibrium state after less than 15 minutes (Figure 1). Shear history
153 can be considered as negligible for digested sludge, but not for raw sludge which undergoes an
154 ageing process.

155 Note that, due to continuous bacterial activity, this ageing process must be considered as a short-
156 term characteristic: fermentation induces a fluidisation of the material (Baudez and Coussot, 2001)

157 and over long experimental times, under constant stress and constant frequency, the shear strain
158 will increase.

159

160 Strain sweep

161 For both raw and digested sludge, G' is nearly constant at low shear strain, suggesting a linear
162 viscoelastic regime (LVE), in agreement with the results of Ayol et al. (2006). Then, both moduli
163 become strain dependent with G' decreasing and G'' passing through a peak before decreasing as
164 well (Figure 2). Of further interest is the strain-dependence of G' and G'' : when $G'' > G'$, they both
165 follow a power-law model (Figure 3), such as:

$$\begin{aligned} G'' &\propto \gamma^{-n} \\ G' &\propto \gamma^{-2n} \end{aligned} \tag{1}$$

167 This peculiar behaviour is known to be the hallmark of soft-glassy materials (Wyss et al., 2005) and
168 has been noticed for many other systems such as colloidal glasses (Mason and Weitz, 1995),
169 emulsions (Mason et al., 1997) and gels (Altmann et al., 2004).

170 However, while the transition from a solid-like to a liquid-like behaviour is smooth with digested
171 sludge, raw sludge suddenly yields: G' is divided by almost 10 and the strain drops sharply from 5
172 to 16% when the applied stress changes from 0.43 to 0.46Pa (Figure 2 and insert).

173 It is also worth noting that the peak in G'' vanishes when the temperature increases (figure 4) and
174 then disappears at very high temperatures for digested sludge while it appears to remain at almost
175 constant amplitude with the raw sludge (figure 5).

176

177 At this point, one can conclude that both raw and digested sludge present similarities with soft-
178 glassy materials, but also some differences:

- 179 - digested sludge appears not to be an “out-of-equilibrium” material (at least at the
180 considered concentration) and tends to behave like a simple colloidal suspension;
- 181 - raw sludge is an out-of-equilibrium material which abruptly yields from a solid-like to a
182 liquid-like behaviour.

183 These differences may be attributed to the degree of dispersion of digested sludge which is 4 times
184 higher than activated sludge, and the EPS concentration which is 2 times lower for digested
185 sludge: according to Mikkelsen and Keiding (2006), the EPS fraction is the most important

186 parameter with respect to floc structure and the presence of large EPS quantities may increase the
 187 interaction via entanglement, which induce relaxation processes (Thurston, 2001).
 188 In both cases, increase of temperature induces a decrease of rheological characteristics: raw and
 189 digested sludge become more and more fluid (Figures 4 and 5) and we emphasise a
 190 proportionality between water viscosity and the strain at the cross-point where $G'=G''$ (Figure 6)
 191 and above. Because water viscosity follows an Arrhenius law with temperature, we can deduce
 192 from Figure 6 that when $G''>G'$, the viscoelastic characteristics follow an Arrhenius law too, with
 193 the same activation energy as water viscosity.
 194 These results suggest that the same molecular movements are involved in the temperature-
 195 dependence of loss modulus and storage modulus in the liquid-like regime and water viscosity.
 196 However, in the solid-like regime, ($G'>G''$), both G' and G'' follow a non-Arrhenius Vogel–
 197 Tamman–Fulcher (VTF) equation with the temperature (Figure 7) with almost the same T_0 (Table
 198 1):

$$199 \quad G' = A \cdot \exp\left(\frac{Ea}{R \cdot (T - T_0)}\right) \quad (2)$$

200 This relation contains three adjustable parameters, A, Ea and T_0 , with T_0 being the temperature
 201 where ‘free volume’ disappears in many ‘free volume’ models. The observed deviation from the
 202 Arrhenius law in the solid-like regime ($G'>G''$) is similar to what it is observed with fragile glasses
 203 (Kobayashi and Takahashi, 2008): when $G'>G''$, raw and anaerobic digested sludge can be seen
 204 as an amorphous solid; but they behave more like disordered liquids when $G''>G'$.

205

206 **Table 1: Parameters of Equation (2) for the raw and digested sludge (at 3.2%) submitted to a constant**
 207 **shear stress respectively equivalent to a 1 and 2% shear strain.**

	G'	G''
Digested sludge		
A [Pa]	9.58	1.58
Ea/R [°C]	35.00	13.77
T_0 [°C]	98.36	97.91
Raw sludge		
A [Pa]	12.75	1.872

Ea/R [°C]	17.10	15.99
T ₀ [°C]	95.02	94.88

208

209 Frequency sweep

210 In the linear regime (shear strain lower than 2%), both raw and digested sludge show a weak
 211 power-law dependence (power law index smaller than 0.1) with the frequency (figure 8) with G' and
 212 G'' in a nearly constant ratio (#0.15). In the highest frequency range the digested sludge presents a
 213 shallow minimum in the G'' curve.

214 In the non-linear regime (shear strain higher than 10%), digested sludge exhibits a plateau for G' at
 215 intermediate frequencies and a localized minimum for G'' (Figure 9) while raw sludge exhibits a
 216 plateau for both G' and G'' (data not shown). At lower frequencies, for both sludges, the loss
 217 modulus varies linearly with the frequency while the storage modulus follows a power-law with a
 218 power-law index higher than 1 which also increases with the temperature, at least for the digested
 219 sludge (figure 9-10):

$$220 \quad G' \propto \omega^n \quad (n > 1), \quad G'' \propto \omega \quad (3)$$

221

222 Moreover, the linearity between frequency and loss modulus at low frequencies suggests
 223 similarities of the behaviour at all temperatures investigated in this work. Unfortunately, as
 224 previously mentioned such an assumption cannot be verified with raw sludge which is a highly
 225 fermentable and continuously changing material: frequency sweep experiments are time
 226 consuming and as the temperature increases, fermentation kinetics also increase. Consequently in
 227 such a case it is simply not possible to assume constant material properties throughout the
 228 experiment. However, with digested sludge, we can make this assumption and by horizontally
 229 shifting the frequency-dependence curves we obtain a master curve (Figure 11) for digested
 230 sludge samples at two different concentrations

231 Surprisingly, the horizontal shift factor presents a linear relationship with the water viscosity for the
 232 lower concentration (Figure 12) but not for the higher concentration, indicating that thermal
 233 agitation cannot be considered as a key factor when the concentration increases. Consequently,
 234 other interactions can no longer be neglected, such as hydrophobic or electrostatic forces
 235 (Mikkelsen and Keiding, 2002).

236

237 Table 2 summarizes the main characteristics of the raw and digested sludge, including results get
238 from the literature. First of all, anaerobic digestion not only modifies sludge composition but also its
239 rheological behaviour. Consequently, these changes have to be taken into account in the flow
240 behaviour analysis of material being digested in order to improve mixing and homogenisation.

241 If we try to establish a parallel with well-known materials, these features (of raw and digested
242 sludge) are similar to those found in the literature regarding the viscoelastic behaviour of soft-
243 glassy materials (Chen et al., 2010). However, soft-glassy materials encompass many materials
244 such as pastes, foams, emulsions, colloids, etc. with their own specific characteristics. Looking at
245 the ageing process; emulsions (Mason and Weitz, 1995) or paints (Baldewa and Joshi, 2011)
246 could be seen as a convenient model for digested sludge. This assumption can be strengthened
247 with the fact that, according to the literature (Forster, 1983), digested sludge is composed mainly of
248 protein and lipopolysaccharides which can be seen as amphiphile materials. Besides, raw sludge
249 highlights a more complex behaviour, with ageing and abrupt yielding, but also with temperature
250 dependence, which is reminiscent of (thixotropic) colloidal gels (Joshi et al., 2008). This last
251 assumption is in agreement with the work of Legrand et al. (1998) and Dursun and Dentel (2009)
252 who considered that the gel approach is a pertinent conceptual model for sludge structure.

253 Even if these assumptions still have to be clearly established, it may signify that during anaerobic
254 digestion sludge evolves from a colloidal gel-like material to an emulsion-like material, and we may
255 have to deal with a mix of emulsion-like and gel-like materials within reactors. Such a complexity
256 may induce a very complex rheological behaviour in terms of mixing and homogenisation
257 (industrial digesters are bigger than 10.000m^3).

258 Thus, further work has to be done by comparing all the rheological characteristics of digested and
259 raw sludge with emulsion or paint and with colloidal gels over a broader range of concentrations;
260 but also by looking at the rheological behaviour of sludge during anaerobic digestion, when all the
261 highlighted characteristics coexist.

262

263

264
265

Table 2: main characteristics of both raw and digested sludge. The symbol * indicates results coming from the literature and cited in the introduction.

	Raw sludge	Digested sludge
Major interactions*	Electrostatic	Steric
Power-law rheology*	Yes	Yes
Shear thinning behaviour*	Yes	Yes
Shear-banding*	No	Yes
Ageing after shear rejuvenation	Yes	No
Temperature dependence (at least in the considered range of solids concentration)	Non-Arrhenius law ($G' > G''$) Arrhenius law ($G' < G''$)	Non-Arrhenius law ($G' > G''$) Arrhenius law ($G' < G''$)
Time-temperature superposition	Unknown	Yes
Strain dependence of G' and G'' (non-linear regime)	Power-law, G'' passes through a maximum before abrupt yielding	Power-law, G'' passes through a maximum before smooth yielding
Frequency dependence of G' and G''	G'/G'' nearly constant (linear regime) $G' \propto \omega^n, G'' \propto \omega$ (non-linear regime)	G'/G'' nearly constant, shallow minimum for G'' (linear regime) $G' \propto \omega^n, G'' \propto \omega$ (non-linear regime)

266

267

268 Conclusion

269

270 The viscoelastic behaviour of raw and anaerobically digested sludge was analysed using
271 oscillatory measurements. We found that both materials present strong similarities with soft-glassy
272 materials: the storage modulus decreases monotonically with the shear strain, while the loss
273 modulus passes through a maximum before decreasing. In the liquid-like regime, when $G' < G''$,
274 both moduli followed a power-law dependency against frequency. Increase of temperature also

275 induced a fluidisation of sludge, with a decrease of rheological characteristics according to both
276 Arrhenius and VTF laws. However, raw and digested sludge have different structure and dominant
277 interactions: also – the ageing process only occurs with raw sludge, not with digested sludge.

278 In the range of concentrations tested, both sludges are temperature dependent and this behaviour
279 appears to be highly dependent of thermal agitation, with some linear relationship between
280 rheological characteristics and temperature-water viscosity variations.

281 We have shown that colloidal gels and emulsion can model the rheological behaviour of
282 respectively raw and digested sludge. Thus, this paper opens a new insight into sludge
283 management by empowering engineers to model digested sludge with emulsions and raw sludge
284 with colloidal gels. However, more work has to be done, by comparing all the rheological
285 characteristics of digested and raw sludge with emulsion or paint and with colloidal gels over a
286 broader range of concentrations.

287

288

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293

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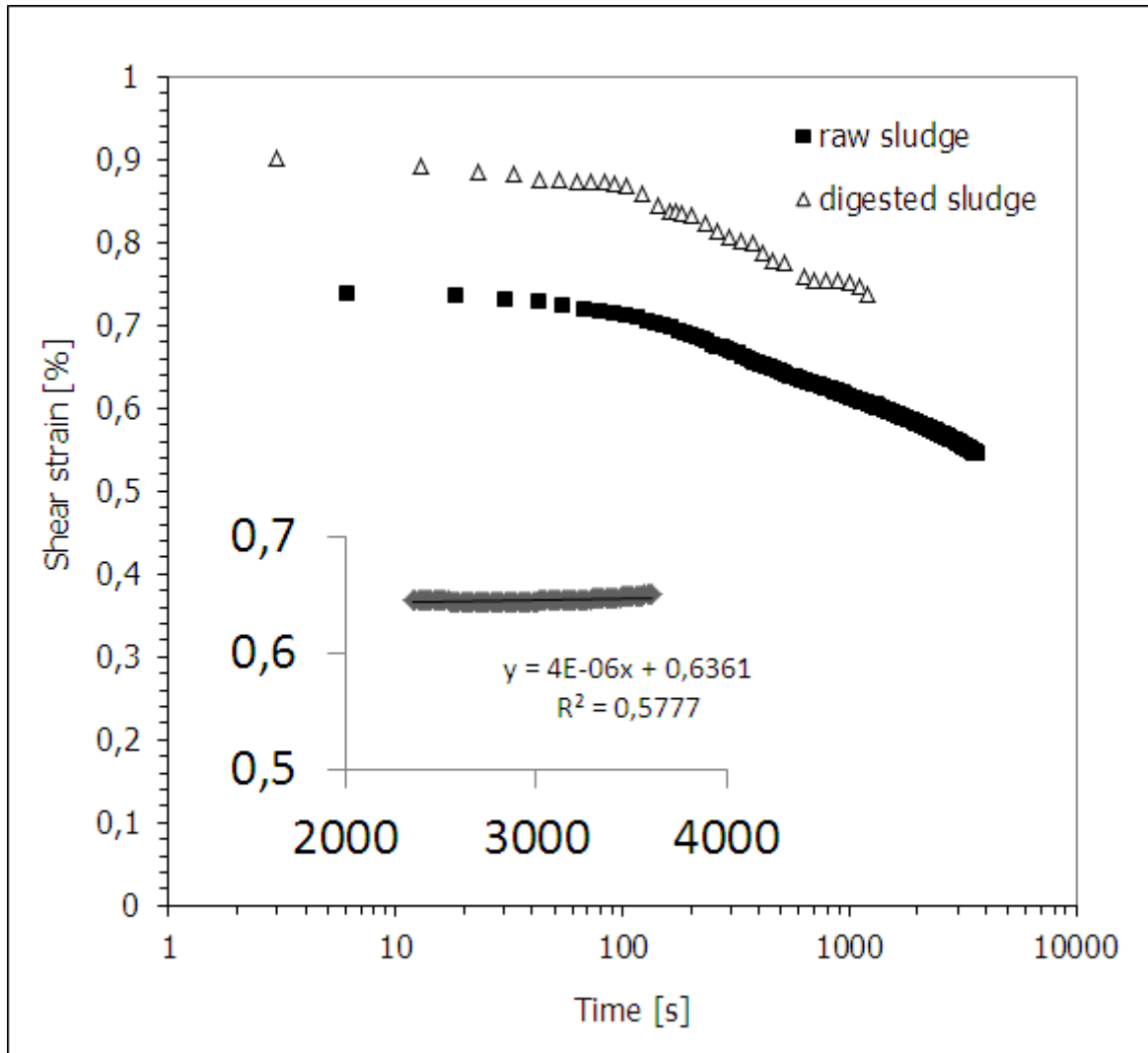
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Figure 1: Time evolution of the shear strain in the linear viscoelastic regime for both digested (at 42 g.L⁻¹) and raw sludge (at 45 g.L⁻¹) when a constant shear stress is applied, respectively equal to 1Pa and 0.65Pa. The insert shows the strain evolution of digested sludge over longer time at a smaller shear stress (0.3Pa) and evidences that shear strain is remaining constant.

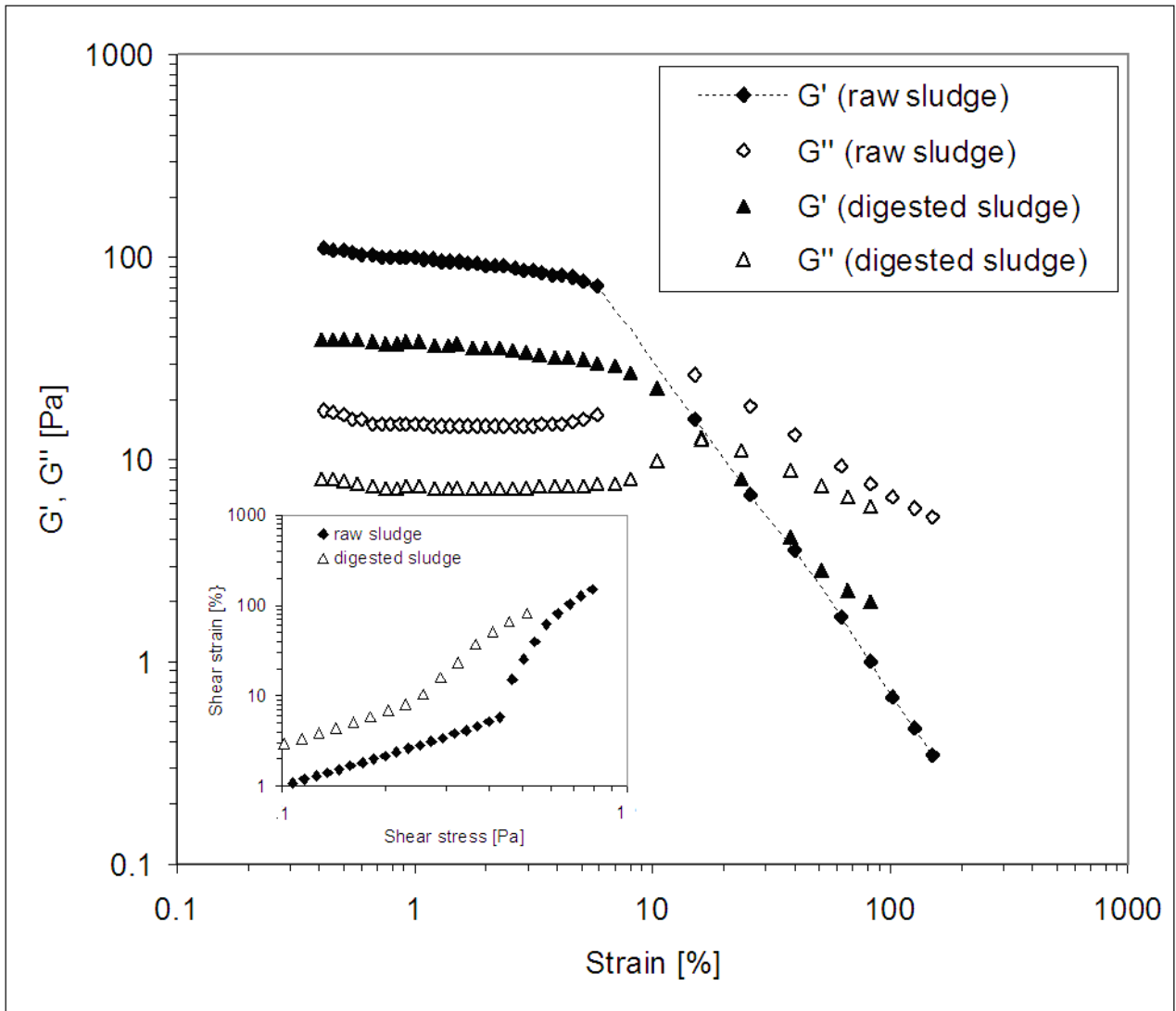


Figure 2: Evolution of storage and loss moduli during stress sweep. The insert shows the stress-strain relationship and the abrupt yielding of raw sludge compared to anaerobic sludge.

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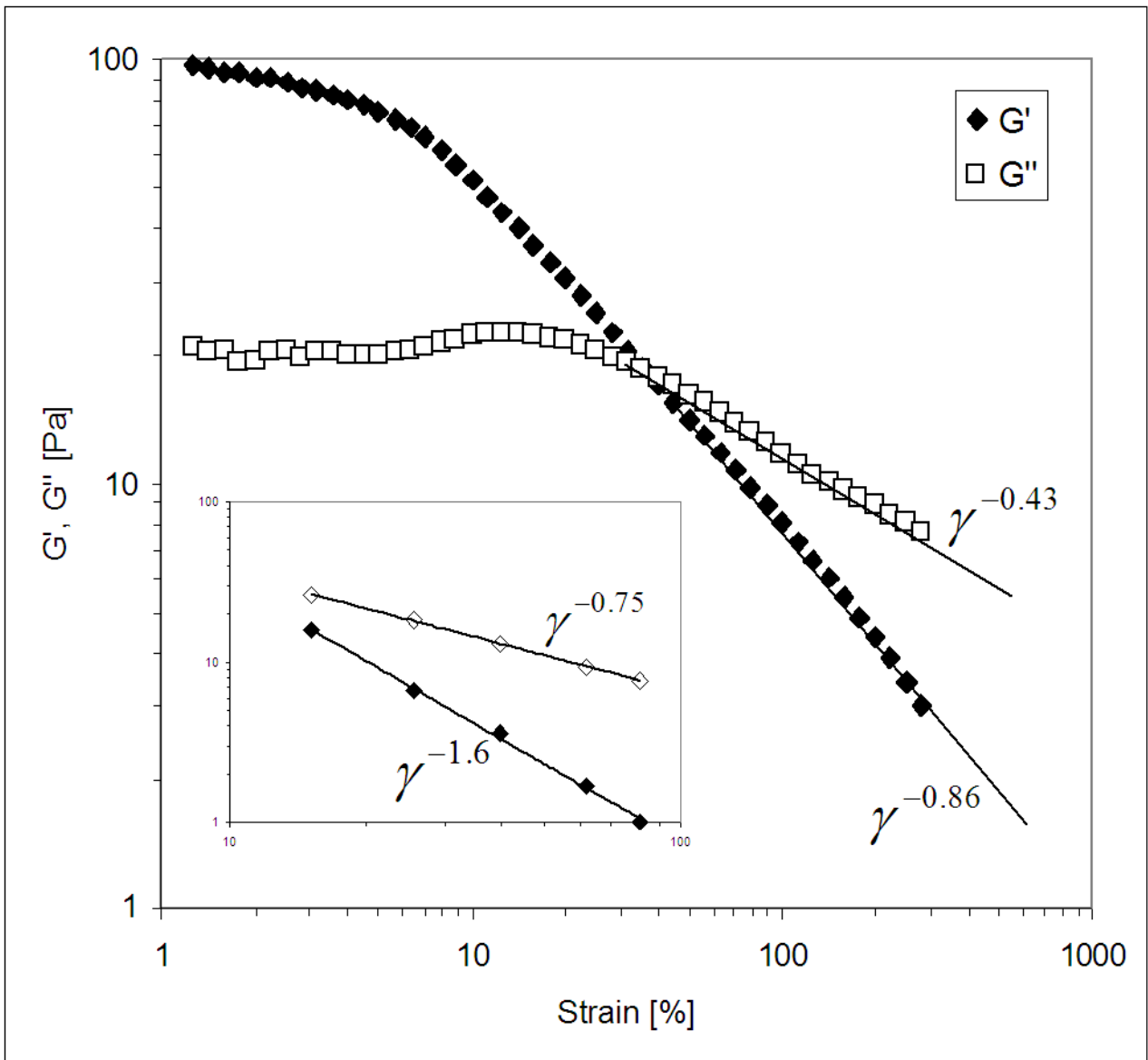


Figure 3: strain dependence of elastic (G') and loss (G'') moduli, at 25°C and 1Hz, for the digested sludge concentration of 3.2%. The insert represents the strain dependence of G' and G'' for the raw sludge in the liquid-like regime.

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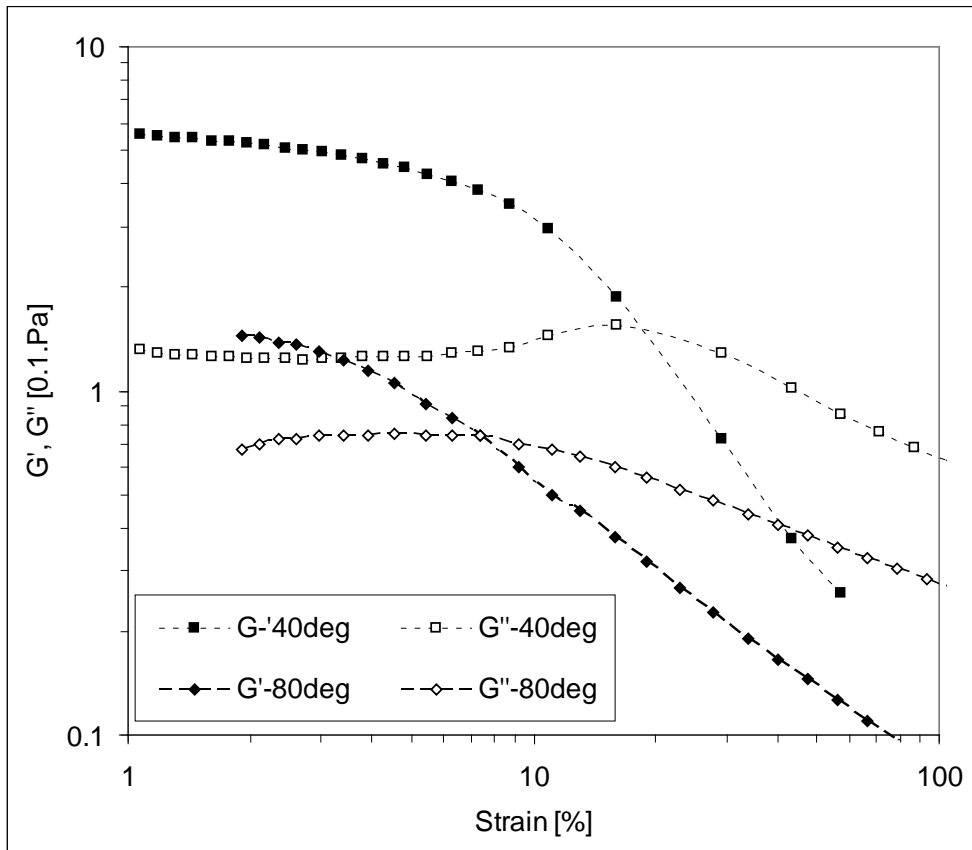


Figure 4: Strain sweep, at 0.2Hz, for a digested sludge concentration of 3.2%

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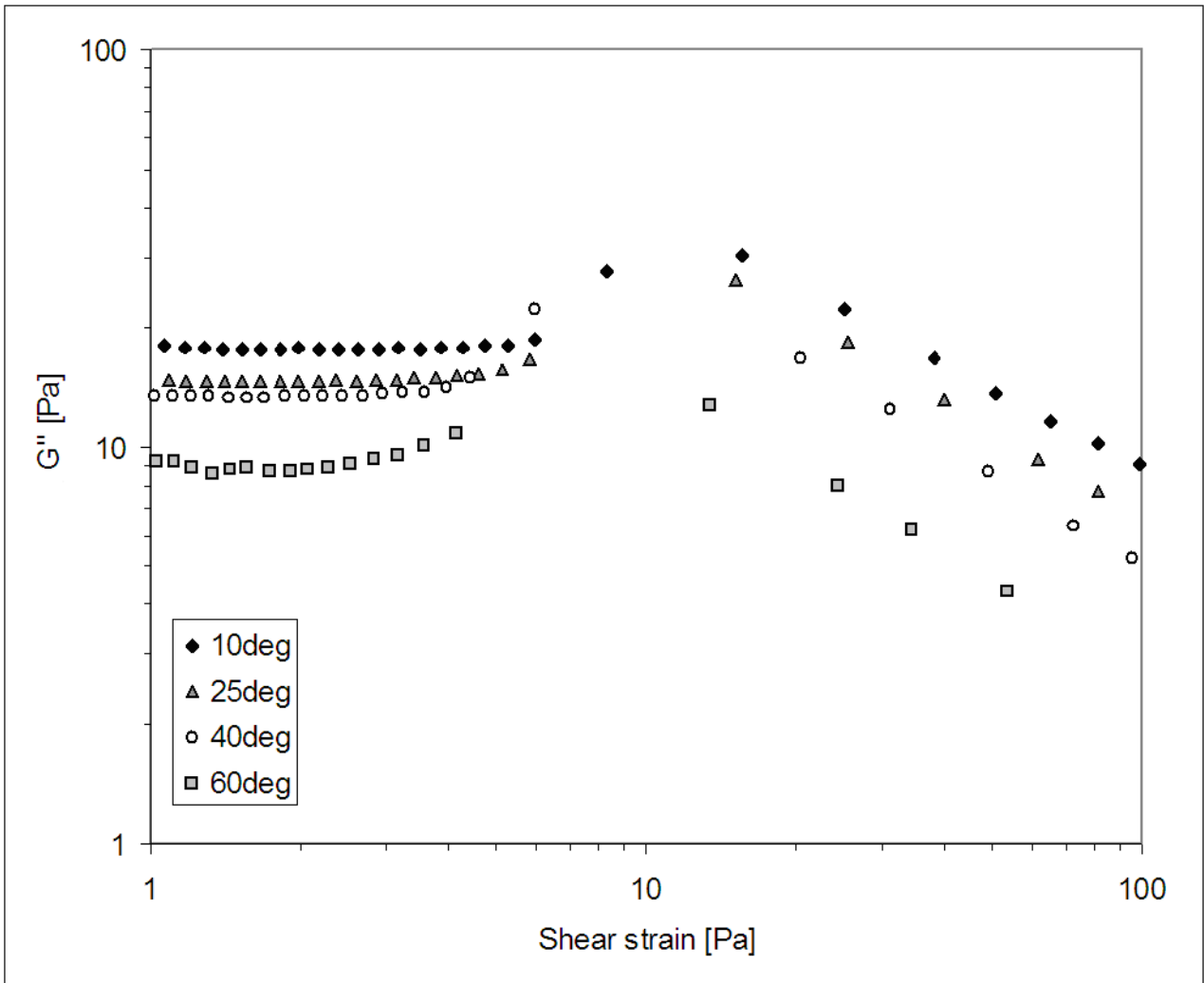


Figure 5: Evolution of G'' at different temperatures during a stress sweep for the raw sludge.

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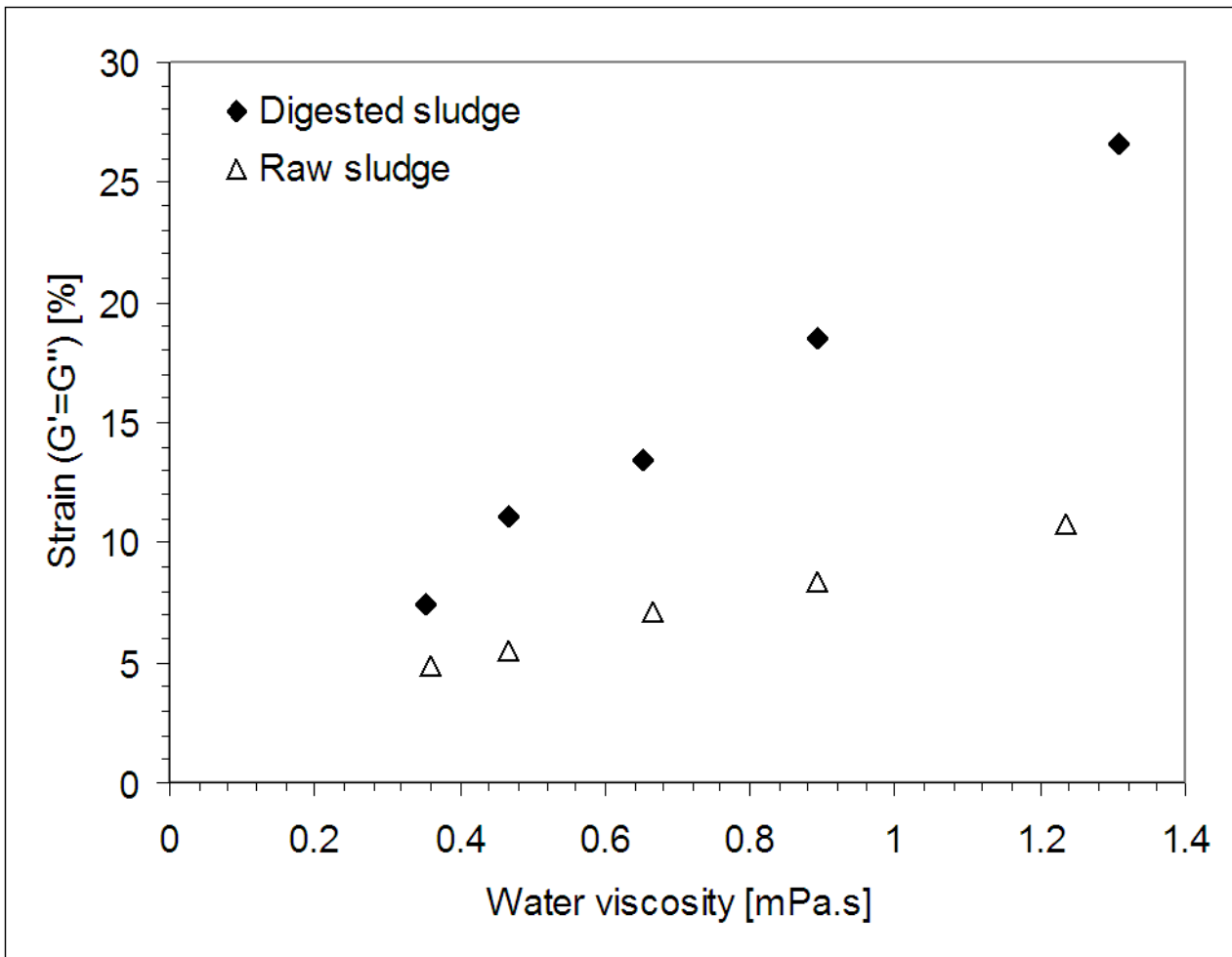


Figure 6: Water viscosity and strain for which $G'=G''$ at 0.2Hz for the digested sludge (at 3.2%) and 0.5Hz for the raw sludge at the 5 temperatures considered (10, 25, 40, 60°C).

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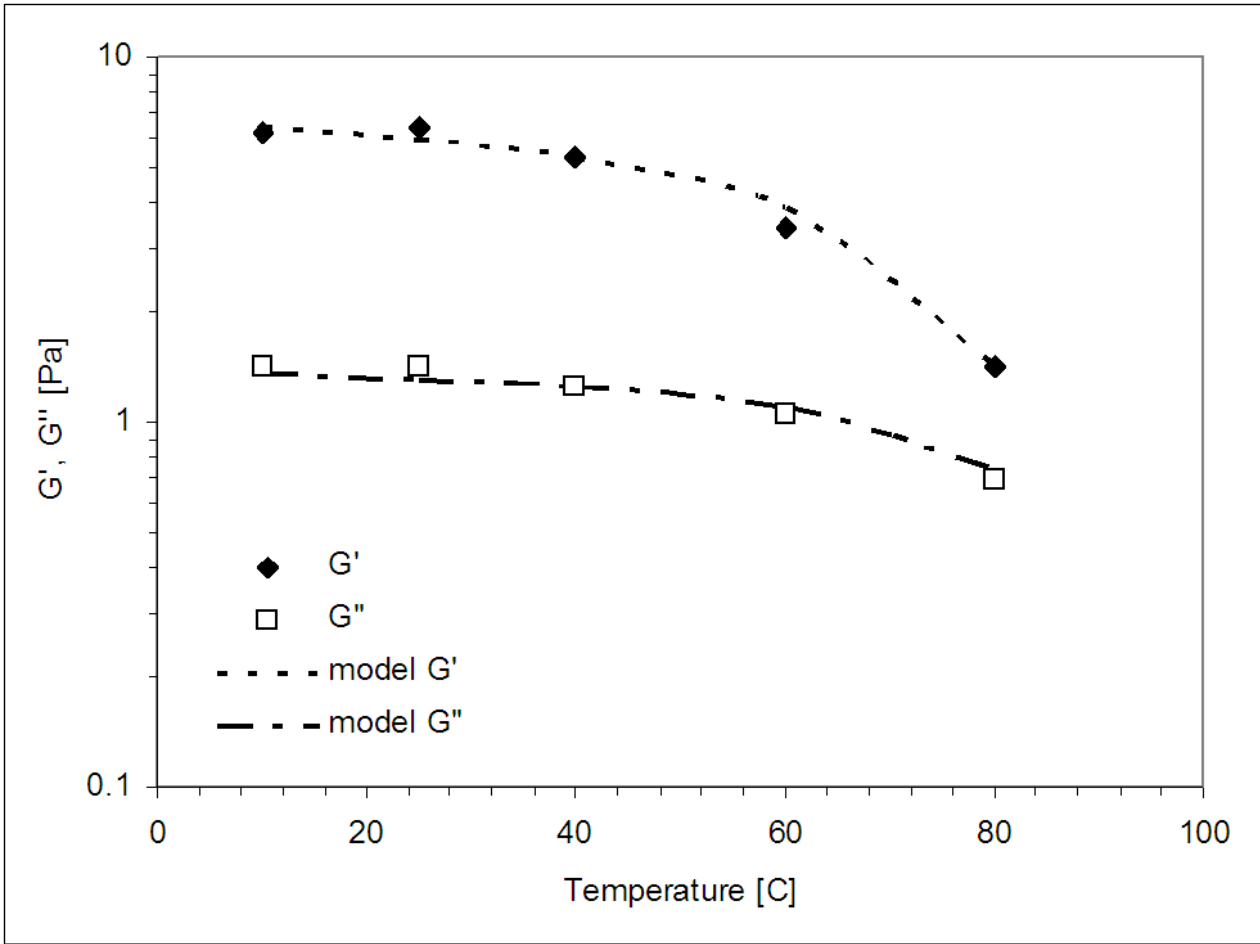
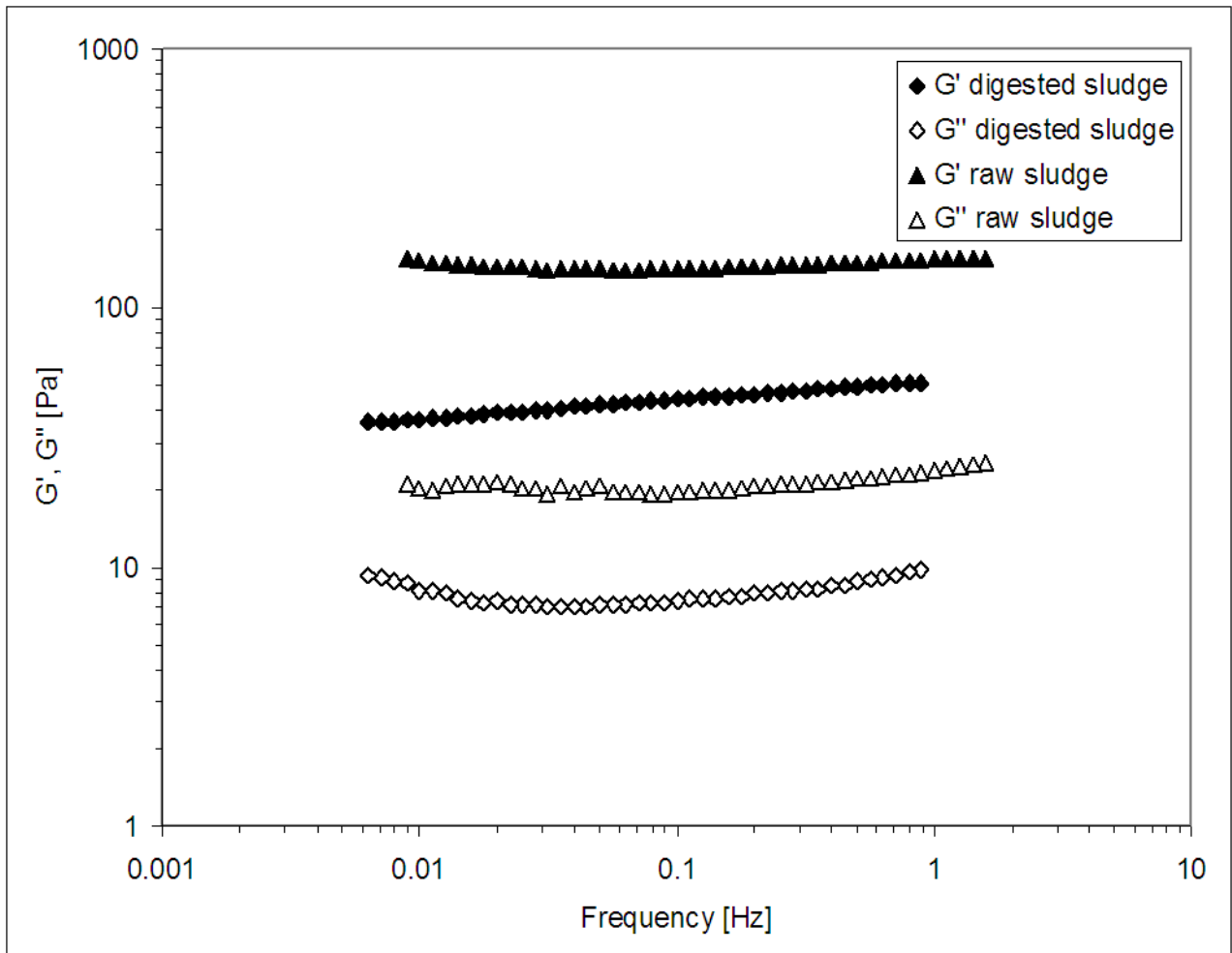


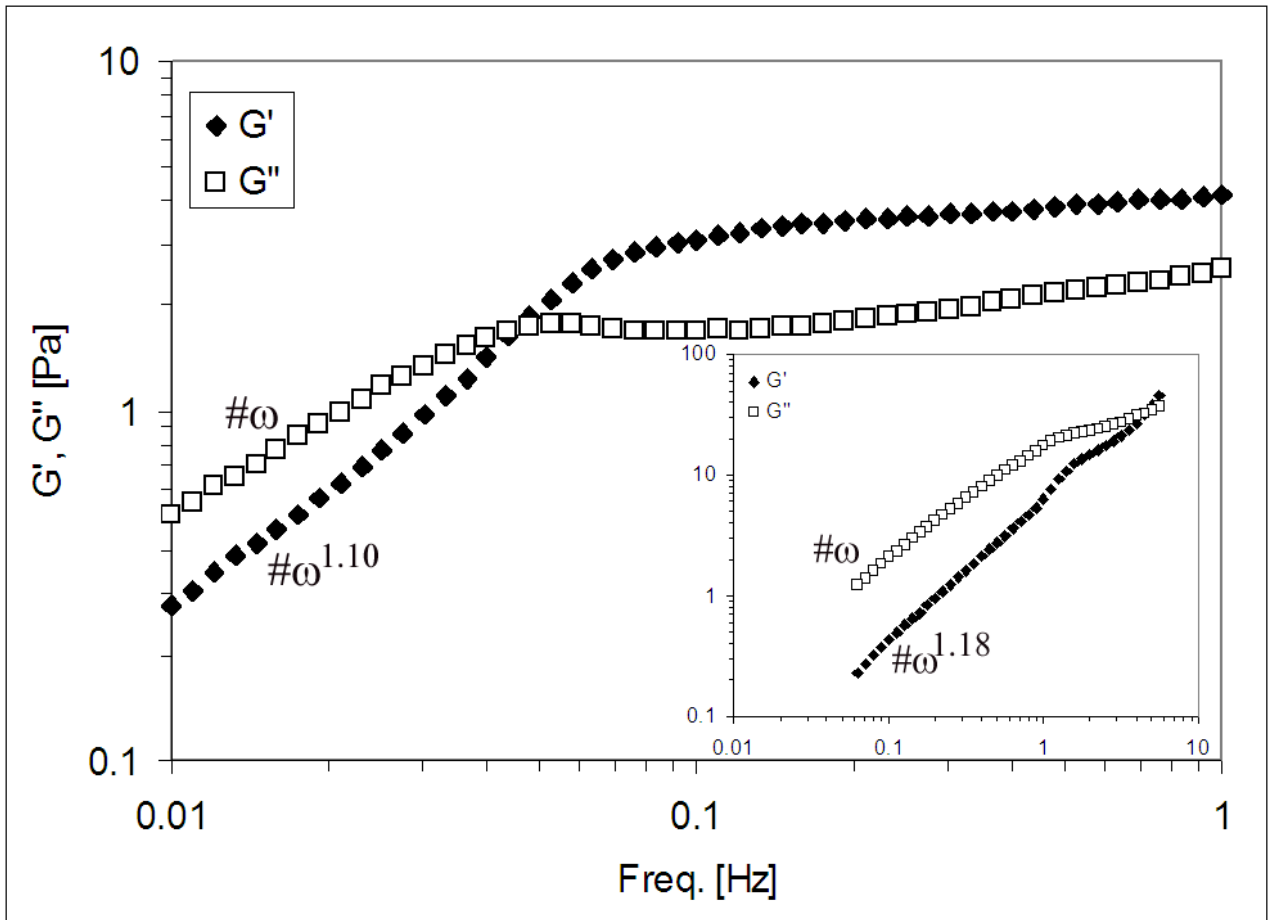
Figure 7: G' and G'' both follow a non-Arrhenius law. Model parameters for the 3.2% sludge submitted to a constant shear stress equivalent to a 2% shear strain at 0.2Hz are respectively $A=12.94\text{Pa}$, $Ea/R=50.43^\circ\text{C}$ and $T_0=98.40^\circ\text{C}$ for G' , $A=1.61\text{Pa}$, $Ea/R=13.77^\circ\text{C}$ and $T_0=97.91^\circ\text{C}$ for G'' .

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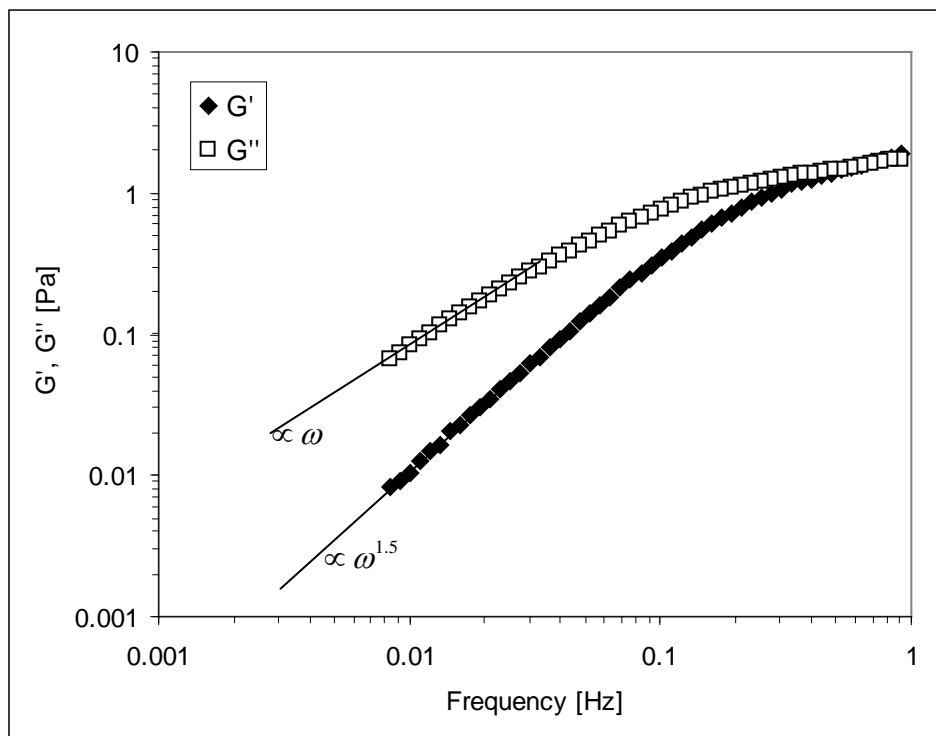
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Figure 8: Frequency sweep in the LVE regime for both sludges. The slight increase of G' and G'' for the raw sludge may be attributed to ageing process



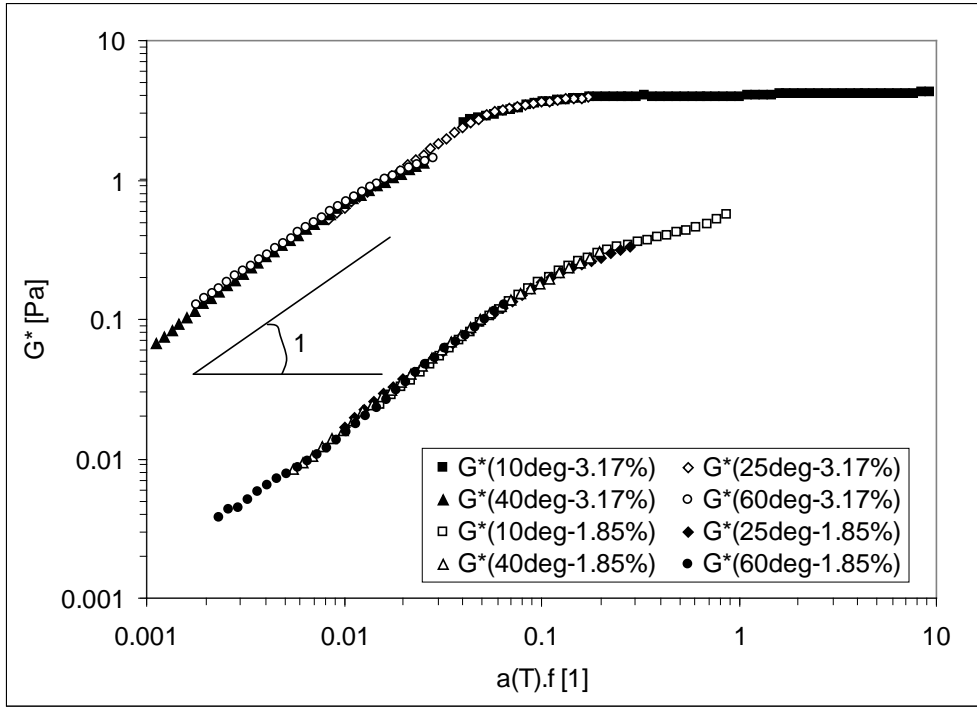
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Figure 9: Frequency-dependence of G' and G'' at 25°C for the digested sludge in the non-linear regime. The insert shows the frequency dependence of raw sludge also in the non-linear regime.

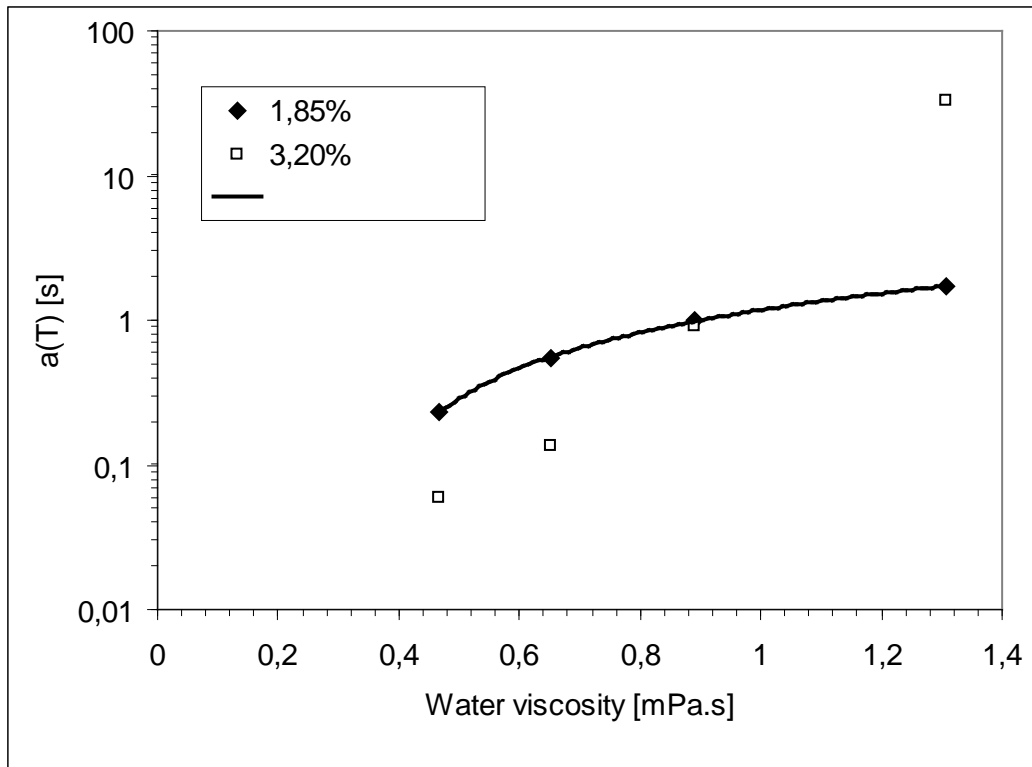


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Figure 10: Frequency-dependence of the digested sludge at 40°C



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Figure 11: Time-temperature superposition of the complex modulus for both concentrations of sludge.



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Figure 12: Horizontal shift factor against water viscosity for the 1.85% and 3.2% sludge. The solid line represents a linear model.