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Laurent Chaunier, Guy Della Valle, Denis Lourdin, Anne-Laure Reguerre, Kévin Cochet, et al.. Viscous sintering kinetics of biopolymer filaments extruded for 3D printing. Polymer Testing, 2019, 77, pp.105873. 10.1016/j.polymertesting.2019.04.020. hal-02352802

HAL Id: hal-02352802 https://hal.science/hal-02352802

Submitted on 25 Oct 2021

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Version of Record: https://www.sciencedirect.com/science/article/pii/S0142941819303216 Manuscript_bb0fa783fa8a06dcc1d28b2d3b11d0d7

1	Viscous sintering kinetics of biopolymer filaments extruded for 3D printing						
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9							

10 Abstract

The characteristic time for viscous sintering of thermoplastics is an important parameter in 11 industrial processes such as welding, rotational moulding but also additive manufacturing. For 12 13 Additive Manufacturing by Material Extrusion (AM-ME), it gives information about spreading dynamics. An experimental setup was designed to characterize the viscous sintering 14 15 of cylindrical filaments (extruded for AM-ME) under controlled thermal conditions. It consists of a small thermally controlled oven, coupled with an image acquisition system to 16 follow-up the coalescing cylinders' cross section shape. The evolution of the bonding angle 17 18 and the convexity index can be calculated to evaluate the temperature dependence of the characteristic time for viscous sintering and the final sintering quality. This approach was 19 applied to glycerol plasticized zein, a biopolymer formulated for AM-ME processing. A 20 processing window (120-130°C) was identified where a high convexity index is reached 21 within a characteristic sintering time close to that of ABS in AM-ME processing conditions. 22

23

24 Keywords

25 Image analysis; Material extrusion; Model; Viscous sintering; Zein

27 **1. Introduction**

The viscous sintering kinetics of thermoplastic polymers has been a key for the understanding 28 and optimization of widely spread industrial processes such as welding and rotational 29 moulding and more recently 3D printing by Selective Laser Sintering (SLS) [1, 2]. In these 30 processes involving spherical particles, the classical model of Frenkel [3] developed for 31 ceramics (and later corrected by Eshelby [4] to satisfy the continuity equation) was first 32 applied: a Newtonian viscous flow under the action of surface tension between two identical 33 spherical objects of initial radius a₀ [m] is generally assumed (Fig. 1). However, an 34 35 experimental study on rotational moulding polymers showed limitations of the Frenkel-Eshelby's model [5]. Thus, a modified model was proposed in order to take into account the 36 variation of the radius *a* during sintering and to extend the description of initial coalescence 37 38 stages [6]:

39
$$\frac{d\theta}{dt} = \left(\frac{a_0 \cdot \mu}{\Gamma}\right)^{-1} \cdot \frac{2^{-\frac{5}{3}} \cos(\theta) \cdot \sin(\theta) \cdot (2 - \cos(\theta))^{\frac{1}{3}}}{(1 - \cos(\theta)) \cdot (1 + \cos(\theta))^{\frac{1}{3}}}$$
 (Eq. 1)

40 Where a(t) [m] and x(t) [m] are respectively the radius of the particles and the radius of the 41 neck (Fig. 1, step 2), which define the bonding angle $\theta(t)$ [rad]:

42
$$\theta = \sin^{-1}\left(\frac{x}{a}\right)$$
(Eq. 2)

43 Eq. 1 is thus governed by the characteristic time for viscous sintering $t_{vs1} = \left(\frac{a_0.\mu}{\Gamma}\right)$ [s]. The 44 surface tension of the polymer melt, Γ [N.m⁻¹], acts as a driving force, whereas the melt 45 viscosity, μ [Pa.s], acts as a limiting one during coalescence.

For sintering of particles of polymers typically used in rotational moulding (HDPE and
LLDPE) under isothermal conditions, the numerical solution of Eq. 1 showed significantly
better predictions than the Frenkel-Eshelby's model [6]. The experimental data were obtained

using an optical microscope equipped with a temperature controlled heat chamber, to monitorthe coalescence of polymer particles placed on a glass plate.

Actually, Eq.1 was later used by its authors to model bond formation between polymer 51 filaments in Additive Manufacturing (AM) by Material Extrusion process (AM-ME, known 52 under the trade name "Fused Deposition Modelling", FDM): The same experimental approach 53 was applied to study the coalescence of thin slices of extruded filaments of ABS, a standard 54 55 amorphous polymer for AM-ME process, under optical microscope [7]. More recently, a different experimental setup was proposed to study the sintering of real filaments of semi-56 crystalline thermoplastic polymers dedicated to AM-ME [8]: two extruded filaments are 57 placed in a transparent oven allowing monitoring the coalescence of the filaments upon 58 controlled heating temperature ramps. In this case, images acquisition (1frame/5s) allowed the 59 measurement of the bonding neck as a function of time. Such experiments validated the 60 61 predictions of the model (Eq. 1) for PLA, the main semi-crystalline polymer used in AM-ME, as well as for PEEK at higher temperature. 62

However, the application of Eq.1 to model bond formation between polymer filaments inAM-ME is questionable for two reasons:

Eq. 1 is supposed to describe the sintering kinetics of spherical particles, not
cylindrical filaments. To our knowledge, the only model for the reliable prediction of
sintering kinetics for two identical cylinders was proposed by Hopper [9]. This model
cannot be expressed in a single differential equation. It is based on the geometrical
description of the two cylinders cross section by an inverse ellipse of constant area.
The author gives the numerical solution in the form of a table of values of:

71
$$\left(\frac{\Gamma \cdot t}{\mu \cdot a_0}, \frac{1}{\sqrt{2}}\right) = \left(\frac{t}{t_{\nu s 2}}, \frac{1}{\sqrt{2}}\right) \nu s. \left(\frac{x}{a_0}, \frac{1}{\sqrt{2}}\right).$$

The $\frac{1}{\sqrt{2}}$ factor actually comes from the assumption that after complete coalescence, a single cylinder of radius $a_f = \sqrt{2}$. a_0 is obtained. Compared to the predictions of the model for spherical particles (Eq. 1) those from Hopper's model for cylinders show similar results at the beginning of sintering, up to $x/a_0 = 0.8$. However, noticeable differences, about 10%, are obtained at the completion of coalescence, with final x/a_0 = 1.41 for Hopper's model and $x/a_0 = 1.26$ when applying Eq. 1 [6]. However, Hopper's model was not used in later works on cylinder coalescence [7, 8].

2) Recent experimental [10] and modelling results [11] suggest that viscous sintering 79 is not the main phenomenon involved in bond formation during AM-ME. Infrared 80 thermography measurements [10] during the process showed that the cooling rate of 81 the deposed filaments is extremely fast (≈ 100 °C/min) and that the temperature at the 82 83 interface between two filaments does not stay above the glass transition temperature more than 1 to 2 s. For that reason, a recent modelling work [11] insists on the role of 84 polymer chain interdiffusion at the interface between filaments (Fig. 1, step 3), which 85 86 occurs much faster that viscous sintering kinetics described by Eq.1, and is known to be a key phenomenon affecting the final quality of the bond adhesion [12]. However, 87 the same authors point out that their model neglects the polymer spreading dynamics 88 at the filaments interface that necessarily precedes and affects chain interdiffusion 89 [11]. Indeed, it is known that spreading dynamics are governed by a same 90 characteristic time $\left(\frac{a_0 \cdot \mu}{\Gamma}\right)$ [13], that is to say the same characteristic time involved in 91

92 viscous sintering
$$t_{vs1}$$
, or $t_{vs2} = \left(\frac{a_0 \cdot \mu}{\Gamma}\right)$ [s].

93 Therefore, while studying viscous sintering kinetics of filaments does not mimic the whole 94 complexity of AM-ME, it provides an interesting way to access the temperature dependence 95 of a characteristic time that is of strong interest in the perspective of a detailed understanding 96 and modelling of this process. So, the present work has the following objectives: 97 - The design of an experimental setup allowing the monitoring of the coalescence of
98 polymer filaments by a camera, at temperatures ranging from the extrusion
99 temperature used in AM-ME, down to significantly lower temperatures.

- The development of an image advanced analysis of the frames taken by the camera
 to sharply characterize the sintering kinetics.
- The identification of the characteristic time for viscous sintering at different
 temperatures by modelling the experimental data by both Eq. 1 (spherical particles
 approximation) and the model of Hopper for cylinders.

This approach is applied to a biopolymer recently pointed out as a candidate for the AM-ME
process and formulated in this purpose: Zein, a protein from corn, with potential applications
as a biomaterial taking advantage of its bioresorbability [14].

108

109 **2. Experimental**

110 2.1. Raw materials and plasticized zein processing

Commercial zein in the powdery state (Ref. Z3625, containing 5% moisture) and glycerol, 111 112 used as a plasticizer, were purchased from Sigma-Aldrich (Saint-Quentin-Fallavier, FR). These materials were mixed in a household kneader (De'longhi Kenwood; Clichy, FR) for 2 113 min at 20 °C, to obtain the formulation based on zein with 20w% glycerol. This mixture was 114 processed with a twin-screw microcompounder (Haake Minilab, Thermo Scientific GmbH; 115 Karlsruhe, DE) at 130 °C, to extrude the plasticized zein through a cylindrical die ($\emptyset_{\text{filament}} = 2$ 116 mm). The extruded filaments were cut as cylinders with a constant length, $L_{filament} = 5$ mm, for 117 subsequent fusion bonding trials. Longer cylinders (20 mm) were also cut for Dynamic 118 Mechanical Analysis. 119

120 2.2. Cylindrical filament sintering experimental setup

The "hardware" experimental setup (Fig. 2-a) is inspired by the design recently described by
Bakrani *et al.* [8] for the sintering of two horizontally adjacent extruded filaments. However,
various parameters have been optimized for the specific objectives of the present work:

124 - The internal dimensions of the oven $(20 \times 10 \times 50 \text{ mm}^3)$ are significantly reduced. 125 Such a small volume of this thermostated chamber allows rapid heating of the cavity 126 machined in a sole parallelepiped aluminium block. The front of the cavity is a 127 transparent glass plate, while the back is equipped with 3 LEDs ($\emptyset_{\text{LED}} = 3.6 \text{ mm}, 6500$ 128 K, 39 lm; OSRAM Opto Semiconductors, Regensburg, DE) mounted in series for 129 backlighting the two cylinders.

130 - A great attention was paid to thermal control and monitoring: the oven was equipped with a temperature controller (Model 1/16 DIN with automated PID, 48 x 48 x 100 131 mm³; RKC Instrument Inc.; Tokyo, JP) and 4 electrical thermal resistances ($Ø_{resistance} =$ 132 6.5 mm and $L_{resistance} = 40$ mm, P = 30 W each; RS Pro Components SAS, Beauvais, 133 FR) embedded at each of the four corners of the oven. The regulation thermocouple 134 (Type T) was located at the middle of the horizontal upper wall of the oven, in contact 135 with the metal surface. A second thermocouple (type K) was located in the medium 136 part of the oven cavity in order to monitor the environment temperature (Toven, [°C]). 137

- A high image acquisition rate was used (1 frame.s⁻¹): A CMOS camera (EXO model, 138 SVS-Vistek GmbH; Seefeld, DE) equipped with a 20 mm length optical extension and 139 a magnifying lens (Computar model 5.6-32 C macroX10; CBC, Cary, NC, US) has 140 been placed in front of the glass window (Fig. 2-b). This camera allows the acquisition 141 at 1 frame.s⁻¹ of contrasted images coded on 8 bits (256 grey levels, as Tagged Image 142 Format files ".TIF") of the cylinders' cross section. The resolution was determined 143 with a Vernier calliper for each sintering sequence. The average value was found at 144 150 pixels.mm⁻¹. 145

146 The experimental procedure involves three successive steps:

i) Setting the desired sintering temperature T_{set} on the temperature controller, from 80 °C to 140 °C. In this interval, it takes about 7 min to reach a stabilized value $T_{oven} = T_{set} \pm 0.1$ °C in the cavity.

150 ii) Introducing the filaments after opening and closing the transparent window. After 151 this opening/closing sequence, the temperature of the cavity slightly decreases but it takes 10 152 to 20 s for the system to stabilize again at $T_{oven} \approx T_{set}$.

153 iii) Starting image acquisition.

For each temperature T_{set} , experimental trials have been triplicated. In order to monitor precisely the temperature of the filaments, a fourth series of experiments was performed in which a thin thermocouple (type K, $\emptyset_{thermocouple} \approx 0.4$ mm) was located inside one of the two filaments, to measure the temperature at the core of the extruded material ($T_{filament}$, [°C]). The filament was finely drilled to its half-length in order to insert the thermocouple tip.

159 2.3. Image analysis

In the initial images, the section of the two extruded filaments and their fusion bonding neck appear as a dark shape on a bright background (Fig. 2-b). An example of their evolution during a sintering sequence at a temperature $T_{set} = 130$ °C is shown on Fig. 3-a.

163 The successive steps of the image analysis involve: (i) the selection of the region of interest 164 (ROI) by cropping the initial image; (ii) the segmentation by image thresholding carried out 165 with ImageJ (free software; National Institute for Health, US), to obtain binary images with 166 one white object on a black background; (iii) the morphological analysis (implemented on 167 Matlab; The MathWorks Inc., Natick, MA, US).

168 The following morphological descriptors have been defined in order to calculate the bonding 169 angle evolution $\theta(t)$ (Eq. 2):

- 170 The minimum vertical length, L_{Min} , equal to 2.*x* (Fig. 1), corresponding to the 171 bonding neck length.
- 172 The two maximum vertical lengths, L_{MaxL} and L_{MaxR} , for the left and right areas, 173 respectively (Fig. 3-b). Their average value, L_{Max} , is used to calculate the equivalent radius of 174 the filaments given by:

175
$$a = \frac{L_{Max}}{2} = \frac{(L_{MaxL} + L_{MaxR})}{4}$$
 (Eq. 3)

176 Application of Eq. 2 gives the bonding angle:

177
$$\theta = \sin^{-1}\left(\frac{x}{a}\right) = \sin^{-1}\left(\frac{L_{Min}}{L_{Max}}\right)$$
(Eq. 4)

178 Additional morphological descriptors were defined in order to calculate a convexity index of

- 179 the system, I_{Convex} (Fig.3-b):
- 180 The left (S_L) and right (S_R) cylinder's areas.
- 181 The convex area, S_{Convex}, corresponding to the whole object of the segmented images.
- 182 It includes S_L and S_R , and the concavities between filaments.
- 183 A sketch depicting S_L, S_R and S_{Convex} is shown on Fig. 3-b. The convexity index, I_{Convex} [-], is
- 184 defined as:

185
$$I_{Convex} = \frac{(S_L + S_R)}{S_{Convex}}$$
 (Eq. 5)

I_{convex} reaches the value 1 if the fusion bonding leads to a perfect welding of filaments,
without any residual concavity between them [15].

188 2.4. Characterization of plasticized zein

Dynamic Mechanical Analysis (DMA, Model 50N-O1dB; Metravib, Lyon, FR) was performed on cylindrical filaments. Prior to DMA trials, extrudates were coated with a silicone-based hydrophobic grease to limit their dehydration. The mechanical active length between the two grips was set at 10 mm and the extrudates were characterized in the tensile mode at 1Hz, with a strain set at 0.1 % and heating rate 3 °C.min⁻¹.

195 **3. Results and discussion**

The typical evolution of the oven and filament temperatures at the start of sintering 196 experiments is shown on Figure 4. At t = 0, the transparent window is closed and temperature 197 (and image) acquisition is started. As stated in the experimental section, it typically takes 10 198 to 20 s for T_{oven} to come back to the regulated T_{set} value. However, it can be seen that it takes 199 200 more time for the filament core to heat up. It was assumed that the system reached steady state for (T_{oven} - T_{filament}) < 5 °C. Typically that corresponds to 35 s at 130 °C, slightly higher 201 than the value of 15 to 20 s, reported in the case of thermomicroscopy trials at 190 °C on 202 203 thermoplastic particles ($\emptyset \approx 0.5 \text{ mm}$) between glass plates [5].

The time dependences of the bonding angle and the convexity index obtained from image morphological analysis are plotted on Figure 5. In order to compare the sintering rates at different temperatures, the slopes $d\theta/dt$ [rad.s⁻¹] were evaluated for t = 35 s (Table 1). This time was chosen on the basis of filament temperature measurements to ensure isothermal steady conditions (Fig. 4). The maximum (final) values of the convexity index (I_{convex_final}) are also reported in Table 1. Three different behaviours can be depicted:

²¹⁰ - For the lowest temperatures (80 °C and 100 °C), the sintering kinetics are very slow ²¹¹ (d θ /dt about 3.10⁻⁴ rad.s⁻¹ and 28.10⁻⁴ rad.s⁻¹, respectively; Table 1) and sintering is far from ²¹² being complete even for long residence times: the final convexity index values, close to 0.9, ²¹³ are reached after more than 800 s (out of the plot range). This means that the concavities ²¹⁴ between the sintered filaments still represent 10 % of the cross section surface, with final ²¹⁵ bonding angles remaining low (θ _{final} < 0.4 and 0.8 rad, respectively; Table 1).

- For the highest temperature (140 °C), sintering appears very fast ($d\theta/dt > 0.06 \text{ rad.s}^{-1}$) (Fig. 5-a and Table 1). However, the convexity index curve (Fig. 5-b) suddenly drops around 30 s. This drop reflects an expansion of the material due to the formation of bubbles because of plasticizer vaporization. The induced variations in filament dimensions lead to a jagged bonding angle curve (Fig. 5-a). It also has to be noted that the values plotted are average values, whereas the standard deviations are very large in this case (Table 1).

²²² - In the interval [120, 130°C], the maximum (final) values of the convexity index are ²²³ close, from 0.972 to 0.987, indicating an almost perfect sintering without residual concavity ²²⁴ and high final bonding angle, $\theta_{\text{final}} > 1$ rad (Table 1). The time necessary to reach this final ²²⁵ state decreases with temperature, while sintering rates show a threefold increase (from about ²²⁶ 0.011 to 0.036 rad.s⁻¹).

These results illustrate the significance of the convexity index obtained from morphological analysis, as a sensitive indicator of the temperature dependence of the sintering quality. It allows detecting expansion problems at higher temperatures, and residual concavity at lower ones.

The values of θ and $d\theta/dt$ at t = 35s in Table 1 can be used to evaluate the characteristic time for viscous sintering t_{vs1} simply by using Eq. 1 [6]. The same determination with Hopper's model [9] requires the calculation of a master curve (Fig. 6): On this curve ($d\theta / d(t/t_{vs2})$) is plotted as a function of θ . The values were calculated from the numerical data $\left(\frac{\Gamma \cdot t}{\mu \cdot a_0} \cdot \frac{1}{\sqrt{2}}\right) =$ $\left(\frac{t}{t_{vs2}} \cdot \frac{1}{\sqrt{2}}\right) vs. \left(\frac{x}{a_0} \cdot \frac{1}{\sqrt{2}}\right) \approx \left(\sin \theta \cdot \frac{1}{\sqrt{2}}\right)$ given in Hopper's article. For each temperature, taking the value of θ at t = 35 s, the value of t_{vs2} is given by the following relation after reporting our experimental data on the master curve:

238
$$\left(\frac{d\theta}{d\left(\frac{t}{t_{\nu s2}}\right)}\right) = t_{\nu s2} \cdot \left(\frac{d\theta}{dt}\right)$$
 (Eq. 6)

The comparison of the characteristic times for viscous sintering obtained with Eq. 1 and Hopper's model master curve, given in Table 1 as the ratio t_{vs1}/t_{vs2} , shows that, except for the lower temperatures (80-100 °C), the assumption that cylinders sintering can be modelled by Eq. 1 developed for spherical particles is quite reasonable.

We have reported the values of the characteristic time for viscous sintering obtained using the 243 Hopper's model, t_{vs2}, on Figure 7. The processing window for fast sintering in AM-ME is 244 shown as a grey area. Figure 7 also shows the main mechanical relaxation associated to the 245 glass transition of plasticized zein filament observed in DMA. At 25 °C, the material is in the 246 glassy state, with a storage modulus E' close to 1 GPa. This modulus decreases with 247 temperature, taking values close to the loss modulus E" which displays a maximum at T_{peak_E"} 248 \approx 45 - 48 °C, close to the glass transition temperature previously determined by differential 249 scanning calorimetry, $T_g = 42$ °C for the same composition [16]. Beyond 75-80 °C, the 250 moduli measurements become unreliable due to creeping. Actually, in a previous rheological 251 252 study on zein plasticized by glycerol, we showed that in this temperature range, the material starts to flow, under shear, the loss modulus being higher than the storage modulus [16]. For 253 lower temperatures, above the relaxation associated to the glass transition, sintering is still 254 255 possible, but slow, with characteristic times much larger than 100 s. For higher temperatures, at 140 °C, the expansion of the material ascribed to plasticizer evaporation perturbs the 256 coalescence. Finally, in the 120-130 °C range, corresponding to T_g + 80-90 °C, the estimated 257 characteristic time for viscous sintering decreases from 82 s to 25 s. 258

The values obtained for the viscous sintering of plasticized zein melt can be compared to 259 those of ABS at its AM-ME processing temperature T = 240 °C. Assuming $|\eta^*|_{ABS_240^\circ C}$ = 260 5100 Pa.s, $\Gamma_{ABS \ 240^{\circ}C} = 29 \text{ mN.m}^{-1}$ and 2.a_{0 ABS \ 240^{\circ}C} = 0.47 \text{ mm} [7, 17], we obtain t_{vs} ABS \ 240^{\circ}C}} 261 \approx 41 s. This value is very close to the one estimated in this study for the characteristic 262 sintering time of plasticized zein. In previous studies, the processability of plasticized zein by 263 AM-ME was first ascribed to its rheological behaviour at 120-130 °C [16], similar to that of 264 ABS at 230-270 °C. This similarity is confirmed for the characteristic time for viscous 265 sintering and suggests that the values of surface tension of the two polymers in the molten 266 state are also close. 267

In future works, the experimental design and image morphological analysis system described 268 269 in the present study could be used to characterize the viscous sintering behaviour of other materials, and especially those developed for AM-ME. Moreover, in the present work, we 270 271 considered only the shape evolution of the two cylinders cross section. As pointed out in the introduction, the quality of the bond obtained by sintering involves polymer chains 272 interdiffusion through the bonding interface (Fig. 1, step 3). The experimental device may 273 actually be used to produce samples for variable sintering times, in order to test the evolution 274 of adhesion with time and temperature. 275

276

4. Conclusions

An experimental setup has been designed for the characterization of viscous sintering between 278 two polymer cylinders. It consists of a small thermally controlled oven, coupled with an 279 280 image acquisition system. The coalescing cylinders' cross section shape is determined as a function of time by morphological analysis. The two key variables monitored are the bonding 281 angle and the convexity index. The knowledge of the evolution of the bonding angle allows 282 quantifying the temperature dependence of the characteristic time for viscous sintering, t_{vs}, 283 while the convexity index, I_{convex}, is shown to be a sensitive indicator of the temperature 284 dependence of the sintering quality. 285

This approach is illustrated in the case of glycerol plasticized zein, a biobased thermoplastic material formulated for Additive Manufacturing by Material Extrusion (AM-ME). A narrow processing window (120-130 °C, corresponding to T_g + 80-90 °C) is identified using the values of t_{vs} and I_{convex} obtained at different sintering temperatures. In this window, the value of t_{vs} for glycerol plasticized zein is close to the one of ABS at its typical AM-ME processing temperature.

293 Acknowledgements

- 294 The authors would like to thank Yannick Madec (University of Nantes, Carquefou), David
- Legland, Patrice Papineau and Roselyne Désirest (INRA, Nantes) for helpful discussions and
- 296 experimental support.

297 **References**

- 298 [1] J. Boyd, W.T.J. West, S. Wu, E.S. Takacs, J. Vlachopoulos, M.R. Thompson, Automated
- image analysis to characterize the melt densification stage of polymer sintering processes,
- 300 Polymer Testing 60 (2017) 242-249.
- 301 [2] L. Xin, M. Boutaous, S.H. Xin, D.A. Siginer, Multiphysical modeling of the heating phase
- in the polymer powder bed fusion process, Additive Manufacturing, 18, (2017).121-135.
- 303 [3] J. Frenkel, Viscous flow of crystalline bodies under the action of surface tension, Journal
 304 of Physics (USSR) 9 (1945) 385- 391.
- 305 [4] J. Eshelby, Discussion of 'Seminar on the Kinetics of Sintering'. Metallurgical
 306 Transactions 185 (1949) 796–813.
- 307 [5] C.T. Bellehumeur, M.K. Bisaria, J. Vlachopoulos, An experimental study and model
 308 assessment of polymer sintering. Polymer Engineering and Science 36(17) (1996) 2198-2207.
- 309 [6] O. Pokluda, C.T. Bellehumeur, J. Vlachopoulos, Modification of Frenkel's Model for
 310 Sintering, AIChE Journal, 43(12) (1997) 3253-3256.
- [7] C. Bellehumeur, L. Li, Q. Sun, P. Gu, Modeling of bond formation between polymer
 filaments in the fused deposition modeling process, Journal of Manufacturing Processes 6
 (2004) 170-178.
- [8] S. Bakrani, F. Chabert, V. Nassiet, A. Cantarel, C. Garnier, Toward improvement of the
 properties of parts manufactured by FFF (Fused Filament Fabrication) through understanding
 the influence of temperature and rheological behaviour on the coalescence phenomenon, AIP
- 317 Conference Proceedings 1896, 040008 (2017), doi: 10.1063/1.5008034.
- [9] R.W. Hopper, Coalescence of Two Equal Cylinders: Results for Creeping Viscous Plane
 Flow Driven by Capillarity, Communications of the American Ceramic Society (1984) C262C264.

- [10] J.E. Seppala, K.D. Migler, Infrared thermography of welding zones produced by polymer
 extrusion additive manufacturing, Additive Manufacturing 12, Part A (2016) 71-76.
- [11] C. McIlroy, P.D. Olmsted, Disentanglement effects on welding behaviour of polymer
 melts during the fused-filament-fabrication method for additive manufacturing, Polymer 123
 (2017) 376-391.
- [12] C.A. Butler, R.L. McCullough, R. Pitchumani, J.W. Gillespie, An analysis of
 mechanisms governing fusion bonding of thermoplastic composites, Journal of Thermoplastic
 Composite Materials 11(4) (1998) 338-363.
- 329 [13] R.S. Crockett, P.D. Calvert, The liquid-to-solid transition in stereodeposition techniques,
- 330 7th Solid Freeform Fabrication (SFF) Symposium, Univ Texas Austin, Conference
 331 Proceedings, (1996) 257-264.
- [14] L. Chaunier, S. Guessasma, S. Belhabib, G. Della Valle, D. Lourdin, E. Leroy, Material
 extrusion of plant biopolymers: opportunities & challenges for 3D printing, Additive
 Manufacturing 21 (2018) 220-233.
- [15] D. Legland, J. Beaugrand, Automated clustering of lignocellulosic fibres based on
 morphometric features and using clustering of variables, Industrial Crops and Products 45
 (2013) 253-261.
- [16] L. Chaunier, G. Della Valle, M. Dalgalarrondo, D. Lourdin, D. Marion, E. Leroy,
 Rheology and structural changes of plasticized zeins in the molten state, Rheologica Acta
 56(11) (2017) 941-953.
- [17] Q. Sun, G.M. Rizvi, C.T. Bellehumeur, P. Gu, Effect of processing conditions on the
 bonding quality of FDM polymer filaments, Rapid Prototyping Journal 14(2) (2008) 72-80.

343 Figure captions

Figure 1. Fusion bonding steps at high temperature between two model circular thermoplastic
particles: 1- intimate contact, 2- apparition of a bonding neck, 3- neck growth due to polymer
diffusion through interface and 4- randomization for long time.

347

Figure 2. Scheme and photos of the experimental sintering device to follow up the coalescence of polymer cylinders: (a) Thermally regulated oven $(20 \times 10 \times 50 \text{ mm}^3)$ equipped with an internal backlighting and a CMOS camera with magnifying lens for image acquisition. (b) Photos of the experimental device and example of cylinders' cross section initial image, at t = 0 s, of a sintering sequence between two zein-based extruded filaments at 130°C with $\emptyset_{\text{filament}} = 2 \text{ mm}$.

354

Figure 3. Successive steps presented for some selected images acquired during 60 s of a typical sintering sequence at 130°C between two zein-based extruded filaments: (a) Acquisition of images in 256 grey levels; after selection of the Region Of Interest (ROI), segmentation by thresholding (binary image); pre-treated images ready for the morphological analysis with the automated identification of each of the two initial filaments sections. (b) Sketch depicting the morphological descriptors S_L, S_R and S_{Convex} used for the calculation of the convexity index, I_{Convex} (Eq. 5).

362

Figure 4. Evolutions of the temperatures in the oven and at the core of zein-based extruded filaments for $T_{set} = 80^{\circ}C$, 100°C and 130°C.

365

Figure 5. Evolutions of the bonding angle, θ [rad], (a) and the convexity index, I_{convex} [-], (b)

367 during the sintering of two zein-based extruded filaments at different temperatures.

Figure 6. Master curve for the Hopper's model and experimental points.

Figure 7. Thermomechanical properties of a zein-based extruded filament assessed by DMA
(E', the storage modulus [Pa] and E", the loss modulus [Pa]) and average characteristic time
for viscous sintering using the Hopper's model (from Table 1). Peak of the loss modulus, E",
is indicated by a black vertical arrow and the processing window by AM-EM is represented as
a grey area.



Figure 1. Chaunier *et al.*





Figure 2. Chaunier *et al.*









Figure 4. Chaunier *et al.*







Figure 6. Chaunier *et al.*





Figure 7. Chaunier *et al.*

397	Table 1. Fusion bonding properties of zein-based extruded filaments (average value ±
398	standard deviation, for three replicates at each temperature set): Final bonding angle, final
399	convexity index, measured values of bonding angle and bonding rate at 35s and estimated
400	characteristic times for viscous sintering, t_{vs1} (issued from Eq.1; [6]) and t_{vs2} [9].

T _{set}	Final bonding	Final convexity	θ at	dθ/dt at	t _{vs1}	t _{vs2}	t_{vs1}
	angle,	index,	t=35s	t=35s	(Eq.1)	(Hopper)	t_{vs2}
[°C]	θ_{final} [rad]	I _{Convex_final} [-]	[rad]	[10 ⁻⁴ rad.s ⁻¹]	[s]	[s]	[-]
80	0.39 ± 0.02	0.900 ± 0.011	0.31 ± 0.07	3.0 ± 0.8	5233 ± 1460	3492 ± 974	1.5
100	0.73 ± 0.14	0.917 ± 0.025	0.29 ± 0.03	28 ± 10.4	599 ± 222	380 ± 141	1.6
120	1.10 ± 0.10	0.972 ± 0.001	0.54 ± 0.21	108 ± 53.5	77 ± 38	82 ± 41	0.9
125	1.19 ± 0.05	0.987 ± 0.001	0.57 ± 0.05	294 ± 84.9	27 ± 8	30 ± 9	0.9
130	1.27 ± 0.01	0.989 ± 0.003	0.48 ± 0.04	364 ± 46.2	26 ± 3	25 ± 3	1.0
140	$1.33 \pm 0.27^*$	-	0.52 ± 0.11	625 ± 404.6	14 ± 9	14 ± 9	1.0

401 *High values of standard deviation at the completion of coalescence for $T_{set}=140^{\circ}C$ are due to the vaporization 402 of the plasticizer creating bubbles and leading to the expansion of the material

1 Graphical abstract



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3 Chaunier *et al*.