Towards unraveling the sintering process of two polystyrene particles by numerical simulations

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Abstract

In this work, we study different rheological and thermal phenomena present during laser sintering of two polystyrene (PS) particles using fully resolved numerical simulations. In our analysis, we varied the laser power, the initial temperature and the thermal convection coefficient, used different rheological descriptions for the flow behavior and in addition studied the effect of the substrate (used in the experiments) on the temperature distribution of the system. Although we are not able to fully describe the results of the experiments with our simulations for the given parameter set, we obtained important insights in the significance of thermal initial and boundary conditions by systematically studying the sintering process.

1 Introduction

There is a rich history of studies dealing with the sintering of polymer particles. Early experimental methods are based on hot-stage microscopy, as used by Kuczynski et al. (1970) on polymethyl methacrylate (PMMA) with varying heating protocols, by both Hornsby and Maxwell (1992) and Scribber et al. (2006) on polypropylene (PP) with a range of molecular weights, by Berretta et al. (2016) on polyetherketone (PEK) and polyetheretherketone

(PEEK) to broaden the range of engineering polymers used for sintering and by Aid et al. (2017) on polyvinylidene fluoride (PVDF) and PMMA. In Bellehumeur et al. (1996, 1998), a heating chamber is used to assess the coalescence of low- and high-density polyethylene (PE). In most experiments the sintering was studied under isothermal conditions. Towards experiments under non-isothermal conditions, Großer et al. (2012) assessed the heat transfer in PE particles that are heated by a laser beam, with a spot size at least ten times larger than the particles.

To describe and predict the coalescence behavior of different materials, various model descriptions are developed. Frenkel (1945) was the first to derive an analytical relation describing the early stage of sintering for Newtonian fluids and Eshelby (1949) corrected this model to satisfy the continuity equation. In this model, a purely biaxial extensional flow is assumed. Hopper (1990) found an analytical solution for the coalescence of two circular domains with viscous flow behavior in 2D. Pokluda et al. (1997) modified the Frenkel model to take conservation of volume into account, enabling the description of larger deformations during coalescence. Towards the modeling of viscoelastic behavior, Bellehumeur et al. (1998) used a steady-state upper-convected Maxwell (UCM) model to extend Frenkel’s approach and Scribber et al. (2006) took transient rheology into account in the description of the coalescence of two viscoelastic particles following the UCM constitutive model. All these models describe the sintering process under isothermal conditions. Besides analytical descriptions and models, numerical methods are used to study viscous and viscoelastic sintering as well. Both models based on the boundary integral method (Kuiken (1990); van de Vorst et al. (1992); van de Vorst and Mattheij (1992); van de Vorst (1993, 1994)) and models based on the finite element method (Ross et al. (1981); Jagota and Dawson (1988, 1990); Martínez-Herrera and Derby (1994, 1995); Zhou and Derby (1998); Hooper et al. (2000); Balemans et al. (2017, 2018, submitted)) have been developed. With these numerical methods, the non-isothermal sintering of viscoelastic fluids can be modeled in both 2D (with and without taking axisymmetry into account) and 3D.

Understanding the sintering of polymers is in particular relevant for selective laser sintering (SLS), which is a 3D printing technique building objects out of polymer powder. If the effects

of various material and processing parameters on the non-isothermal sintering dynamics and mechanical properties of the printed parts are known, the SLS process can be optimized to build products with improved product quality. Recently, a new experimental setup is developed by Hejmady et al. (2019a,b). This setup makes it possible to quantify laser sintering of a variety of polymeric materials, either amorphous or semi-crystalline while varying process conditions relevant for SLS.

In this work, we limit ourselves to the experimental results obtained for the sintering dynamics during laser sintering of polystyrene which is an amorphous polymer, as presented in Hejmady et al. (2019a). The experiments include a thorough material characterization and the effect of particle size, heating chamber temperature, laser pulse duration and laser energy on the sintering process of two polymer particles are studied using a non-isothermal experimental protocol. We compare the results of our computational model with the presented experimental results, including additional experiments on thermal imaging. This comparison allows to provide insight in the relevance of various material and processing parameters.

2 Experimental setup and measuring method

The experimental setup of Hejmady et al. (2019a,b) is used to perform in-situ visualization of laser sintering of two equally sized polystyrene particles. The two polymer particles are placed on a mirror polished stainless-steel sample substrate which is located inside an aluminum sample chamber of $30 \times 30 \times 30 \text{ mm}^3$. Both the substrate and chamber are kept at a specified temperature using heating rods and thermocouples and insulation prevents heat losses to the environment. From the top, a **fixed** laser beam is guided into the sample chamber. The laser source has a Gaussian intensity distribution at a wavelength of 532 nm, which is in the visible spectrum. The laser beam is pulsed by means of an acousto-optic modulator. The sample chamber allows for optical imaging from the top. In addition, in the present work, infrared imaging from the side is used to characterize the temperature profile in the particles as a function of time. For this, we used an Optris PI640 IR camera with lens. This results in a pixel size of $31 \times 31 \mu\text{m}^2$ at the used working distance. The used emissivity is 0.85 and the

Figure 1: Example of an optical image of two particles at the start of the sintering experiment.

calibration of the camera is verified by measuring the temperature of a polymer bead on a temperature-controlled heating bed.

The spherical polymer particles are made of polystyrene (PS) containing 2 wt% nubian black dye to enable the absorption of visible-light laser energy. With non-destructive micro-manipulation, two powder particles of approximately equal size can be positioned next to each other. After heating the chamber, substrate and particles at low heating rate to the required temperature T_∞ , the setup is ready for the sintering experiment.

Initially the powder particles are at the same temperature as the chamber and the substrate $T(t = 0) = T_\infty = 53^\circ\text{C}$. The **fixed** laser beam with beam radius $W = 20\ \mu\text{m}$ is switched on at time $t = 0\text{ s}$ for a pulse duration of $t_b = 0.8\text{ s}$ with pulse energy $E_p = 28\ \mu\text{J}$ **and is positioned at the point where the two particles touch**. The sintering process is optically visualized in real-time from the top and from this data the evolution of the liquid bridge between the two particles can be determined in time. An example of such an optical image is shown in Figure 1. Simultaneously, the temperature profile of the particles is measured from the side.

In Hejmady et al. (2019a), the energy per pulse was measured with a Gentec QE12 pyroelectric based energy meter with a precision of $0.5\ \mu\text{J}$. To allow more accurate comparison with numerical simulations, we first determined how this energy in the visible spectrum is converted into heat energy absorbed by the polymer in the present work. For this, a thin PS polymer sheet with a thickness of $100\ \mu\text{m}$ was exposed to a laser pulse with pulse energy $E_p = 25\ \mu\text{J}$. Note that this value is slightly lower than the pulse energy used in the sintering experiments. The laser pulse was sent along the plane of the sheet and centered at the middle

Figure 2: Thermal image of temperature distribution in a PS sheet with a thickness of $100\text{ }\mu\text{m}$, exposed to a laser pulse with pulse duration $t_b = 0.8\text{ s}$ and pulse energy $E_p = 25\text{ }\mu\text{J}$ in an environment at $T_\infty = 23^\circ\text{C}$, taken at $t = 0.8\text{ s}$. The grid indicates the different regions used for the determination of the thermal energy from Eq. (1).

of the $100\text{ }\mu\text{m}$ thick side. Figure 2 shows the temperature distribution in the sheet at the end of the laser pulse at time $t = 0.8\text{ s}$, as obtained from IR imaging. We quantified the temperature profile by dividing the heated region in 60 zones. Then, the total heat energy absorbed by the polymer sheet is determined as

$$Q = \sum_{i=0}^8 \sum_{j=0}^5 Q_{ij}, \quad (1)$$

with

$$Q_{ij} = m_{ij} c_p \Delta T_{ij}. \quad (2)$$

Herein, Q_{ij} is the extra thermal heat energy of region ij , m_{ij} its mass, c_p the specific heat capacity and ΔT_{ij} the temperature increase of region ij . Since the PS sheet is very thin, a constant temperature across its thickness is assumed. The temperature profile in Figure 2 shows that this is a reasonable approximation for a first estimate of the laser pulse energy. Applying Eq. (1) results in a total energy of $87\text{ }\mu\text{J}$, which is much higher than the $25\text{ }\mu\text{J}$ measured with the pyroelectric energy meter.

3 Computational method

3.1 Governing equations

We use a 2D geometry of two circular particles as is introduced in Balemans et al. (2018), shown in Figure 3. The contact line L is measured from the origin $(0, 0)$ to the outer boundary. To match the initial contact radius of Figure 1, we use an initial prescribed contact line $L_p = 12.5 \mu\text{m}$.

Figure 3: Geometry of the two circular particles (a) schematic and (b) initial domain.

We use the framework based on the finite element method as described in Balemans et al. (2018, submitted), where we solve the momentum balance, mass balance and energy balance on a moving domain to describe the sintering process of two viscous particles

$$-\nabla \cdot (-p\mathbf{I} + 2\mu(T)\mathbf{D}) = \mathbf{0} \quad \text{in } \Omega, \quad (3)$$

$$\nabla \cdot \mathbf{u} = 0 \quad \text{in } \Omega, \quad (4)$$

$$\rho c_p \frac{DT}{Dt} = k \nabla^2 T + 2\mu(T)\mathbf{D} : \mathbf{D} + Q(x, y, t) \quad \text{in } \Omega, \quad (5)$$

where $D()/Dt$ denotes the material derivative, p is the pressure, $\mu(T)$ the temperature-dependent viscosity, $\mathbf{u}$ the velocity, ρ the density, c_p the specific heat capacity, T the temper-

ature, t the time, k the thermal conductivity, Q a source term and $\mathbf{D} = (\nabla \mathbf{u} + (\nabla \mathbf{u})^T)/2$. Because we study the sintering of polystyrene (PS), an amorphous polymer, we do not have first order phase transitions. Therefore, it is sufficient to use an energy balance without latent heat term. In this work, we present the values of the temperature in $^{\circ}\text{C}$, while we use absolute temperature values in all calculations. Considering dimensionless numbers, we find that the viscous dissipation term is negligibly small, following from the calculation of the Brinkman number $\text{Br} = \gamma^2/(\mu_c k \Delta T_c) = \mathcal{O}(10^{-6})$. Herein, μ_c is the characteristic viscosity at charactersitic temperature $T_c = 123.6^{\circ}\text{C}$ and $\Delta T_c = T_c - T_{\infty}$ the characteristic temperature difference, with T_{∞} the ambient temperature. However, we solve the set of equations as given in Eqs. (3) to (5) to stay in line with previous work.

The laser beam with a Gaussian intensity distribution that heats up the system is prescribed as a volumetric source term Q in this work and will be defined later. As soon as the temperature reaches the glass transition temperature T_g , the polymer liquefies. During the sintering process of two particles, the temperature is leading in the determination of the viscosity, while the effect of shear is of minor importance because of low shear rates. Following Hejmady et al. (2019a), the temperature-dependent viscosity follows the Williams-Landel-Ferry equation

$$\mu(T) = \mu_{\text{ref}} 10^{\left(\frac{-C_1(T-T_{\text{ref}})}{C_2+(T-T_{\text{ref}})}\right)}. \quad (6)$$

Herein, μ_{ref} is the viscosity at reference temperature T_{ref} and C_1 and C_2 are fitting parameters. For temperatures below the glass transition temperature T_g the viscosity goes to infinity

$$\mu(T < T_g) \rightarrow \infty. \quad (7)$$

All other material and process parameters are taken from Hejmady et al. (2019a), are assumed to be independent of temperature and are summarized in Table 1.

From the moment the polymer is in the liquid state, the fluid begins to flow and the domain starts to move. We track the motion of the boundary Γ in a Lagrangian based way.

Therefore, the velocity of the boundary is defined as

$$\frac{d\mathbf{x}_\Gamma}{dt} = \mathbf{u}, \quad (8)$$

where $\mathbf{x}_\Gamma$ are the coordinates of the boundary and $\mathbf{u}$ is the velocity at the boundary Γ .

The driving force of the motion of the domain is the prescribed surface tension γ

$$(-p\mathbf{I} + 2\mu(T)\mathbf{D}) \cdot \mathbf{n} = \nabla_s \cdot (\gamma\mathbf{I}_s) - p_{\text{out}}\mathbf{n} \quad \text{on } \Gamma. \quad (9)$$

Herein, ∇_s is the surface gradient operator, $\mathbf{I}_s = \mathbf{I} - \mathbf{n}\mathbf{n}$ the second-order unit surface dyadic tensor and p_{out} the outside pressure. The outside pressure does not play a role, because we assume that the fluid is incompressible and the material properties are independent of pressure. Therefore, we take $p_{\text{out}} = 0$ in the remainder of this work.

Rigid body motion is prevented by restricting the motion

$$\mathbf{u} = \mathbf{0} \quad \text{at } (0, 0), \quad (10)$$

$$u_x = 0 \quad \text{at } (0, L). \quad (11)$$

The system cools down via a convection-radiation boundary condition

$$-k\nabla T \cdot \mathbf{n} = h(T - T_\infty) + \sigma_B \varepsilon (T^4 - T_\infty^4) \quad \text{on } \Gamma, \quad (12)$$

with h the convective heat transfer coefficient or in short ‘convection coefficient’, T_∞ the ambient temperature, σ_B the Stefan-Boltzmann constant and ε the surface emissivity. Note, that both T and T_∞ are absolute temperatures. Following Hejmady et al. (2019a), the temperature of the domain Ω is initially equal to the ambient temperature $T(t = 0) = T_\infty$.

From the pulse energy E_p and pulse duration t_b , the laser power P can be calculated

$$P = \frac{E_p}{t_b} = 35 \mu\text{W}. \quad (13)$$

Table 1: Material and process parameters for the sintering of PS.

Parameter	Symbol	Value	Notes
Density	ρ	1040 kg/m ³	
Surface tension	γ	35.6 mN/m	
Glass transition temperature	T_g	62 °C	
Specific heat capacity	c_p	1.32 kJ/(kg · K)	
Thermal conductivity	k	0.167 W/(m · K)	
Surface reflectivity	ζ_R	0.05	
Transmittance	ζ_T	0.02	$l = 175 \mu\text{m}$
Convection coefficient	h	50 W/(m ² · K)	
Surface emissivity	ε	0.95	
Particle radius	R	60 μm	
Absorption coefficient	α	22.06 mm ⁻¹	$\zeta_T = (1 - \zeta_R) \exp(-\alpha l)$
Reference viscosity	μ_{ref}	2119 Pa · s	$T = T_{\text{ref}}$
Reference temperature	T_{ref}	100 °C	
WLF constant 1	C_1	10.37	
WLF constant 2	C_2	185.07 °C	
Ambient temperature	T_∞	53 °C	
Beam width	W	20 μm	$I(x = W) = I_0 \exp(-2)$
Pulse energy	E_p	28 μJ	
Pulse duration	t_b	0.8 s	
Beam position	x_b	0	
Stefan-Boltzmann constant	σ_B	$5.67 \cdot 10^{-8} \text{ W}/(\text{m}^2 \cdot \text{K}^4)$	
Gas constant	R_g	8.31 J/(mol · K)	

3.2 Transition from 3D parameters to 2D

Because we use a 2D geometry, we need to take the scaling parameters into account as introduced in Bailemans et al. (submitted). The laser beam with Gaussian distribution in 2D is defined as

$$Q(x, y) = \alpha(1 - \zeta_R)I_0^{2D} \exp\left(-2\frac{(x - x_b)^2}{W^2}\right) \exp(-\alpha(y_\Gamma - y)), \quad (14)$$

with 2D peak intensity

$$I_0^{2D} = \frac{P^{2D}}{\sqrt{\pi W^2/2}}. \quad (15)$$

Herein, α is the absorption coefficient, ζ_R is the surface reflectivity, x_b is the x -coordinate of the center of the incident beam, W is the ‘beam width’ analogous of the beam radius (i.e.

measured from the beam axis to the point where $I(x) = I_0 \exp(-2)$ of the 2D laser ‘sheet’, P^{2D} is the 2D laser power and the distance in y -direction to the boundary Γ is given by $y_\Gamma - y$ with $y_\Gamma \geq 0$.

Next, we need to compute the laser power P^{2D} in 2D that is necessary to reach the same average increase in temperature ΔT as is reached in the experiments using

$$P^{2D} = \frac{P f_e}{(4/3) R f_e^{2D}}, \quad (16)$$

with f_e and f_e^{2D} the fractions of the total laser power that are effectively stored in 3D and 2D, respectively. Because of possible reflections from the substrate in the experiments, we assume that all energy is effectively stored inside the domain and $f_e = 1$. Following the calculation steps as given in Balemans et al. (submitted), we compute $f_e^{2D} = 0.6291$. Calculating Eq. (16), we find that the laser power in 2D needs to be $P^{2D} = 0.695 \text{ W/m}$.

Finally, we have to account for the difference between the ratio of surface to volume (3D) and ratio of boundary to area (2D) in the convection-radiation temperature loss term by means of a correction factor f_{cool}

$$-k \nabla T \cdot \mathbf{n} = (h(T - T_\infty) + \sigma_B \varepsilon (T^4 - T_\infty^4)) f_{\text{cool}} \quad \text{on } \Gamma. \quad (17)$$

Following the calculation steps as given in Balemans et al. (submitted), we compute $f_{\text{cool}} = 1.59$.

3.3 Numerical method

We solve the governing equations with the appropriate boundary conditions using an in-house code based on the finite element method (Hulsen (2019)). The computational domain is discretized using isoparametric, triangular P_2/P_1 (Taylor-Hood) elements for the velocity/pressure and isoparametric, triangular P_2 elements for the temperature. The full procedure is described in Balemans et al. (2018).

4 Results

4.1 Experimental results

In Figure 4, top view optical images of the sintering of two PS particles with radius $R = 60 \mu\text{m}$ are shown for different time points. Based on these images, the dynamics of the contact radius as a function of time is determined and is shown in Figure 5. It can be seen that the dynamics of the contact radius is well reproducible with the corresponding experiment in Hejmady et al. (2019a).

Figure 4: Image sequence with top view optical images of a sintering experiment with particle radius $R = 60 \mu\text{m}$, heating chamber temperature $T_\infty = 53^\circ\text{C}$, pulse energy $E_p = 28 \mu\text{J}$ and pulse duration $t_b = 0.8 \text{ s}$.

Figure 6 shows the temperature distribution at different time points during sintering. This figure clearly shows that the heat energy diffuses rather quickly from the laser illuminated region to the remainder of the particles. This is expected based on the characteristic time for heat diffusion ($t_{\text{diff}} = (2R)^2 \rho c_p / k$), which is approximately 0.1 s. However, a clear temperature gradient across the particles can be noticed, which means that heat conduction inside the particles is more difficult than the further convection in air or conduction in the metal substrate.

Based on the images in Figure 6, Figure 7 presents the temperature in the region of the liquid bridge as a function of time, as this is the relevant region for the sintering process. The

Figure 5: The evolution of the contact line in time for experiments with particle radius $R = 60 \mu\text{m}$, heating chamber temperature $T_\infty = 53^\circ\text{C}$, pulse energy $E_p = 28 \mu\text{J}$ and pulse duration $t_b = 0.8 \text{ s}$.

maximum temperature of 114°C corresponds rather well with the value of 123.6°C obtained from the fit of the evolution of the dimensionless contact radius with the Frenkel model in Hejmady et al. (2019a). Moreover, this temperature is reached within a time $t = 0.1 \text{ s}$, after which more or less isothermal sintering occurs. The comparison between the temperature profile and the sintering kinetics also illustrates that even though the temperature remains constant over the remainder of the laser pulse, the sintering is halted far before the end of the pulse.

4.2 Viscous material

We used the method and parameter values as described above to simulate the experiment of which the results are presented in Figure 5. In Figure 8, the computed evolution of the contact line is shown in time together with a set of experimental data points. As can be seen, there is a large difference in sintering behavior between the experiments and simulations. Whereas the contact line starts to increase immediately upon turning on the laser beam in the experiments, the contact line does not change at all in the simulations. The highest value of the temperature computed in the simulation is $T = 59.7^\circ\text{C}$ at time $t = 0.8 \text{ s}$. Because this value is below the glass transition temperature T_g , the viscosity $\mu(T) \rightarrow \infty$, no material starts to flow and the contact line does not increase. It seems that there is too much heat loss in the simulations.

Figure 6: Image sequence with side view thermal images of a sintering experiment with particle radius $R = 60 \text{ }\mu\text{m}$, heating chamber temperature $T_\infty = 53 \text{ }^\circ\text{C}$, pulse energy $E_p = 28 \text{ }\mu\text{J}$ and pulse duration $t_b = 0.8 \text{ s}$.

From a simulation without heat loss to the environment ($-k\nabla T \cdot \mathbf{n} = 0$), shown in Figure 9, it follows that the maximum temperature $T = 65.8 \text{ }^\circ\text{C}$ is reached at time $t = 0.8 \text{ s}$. Although this value is above the glass transition temperature T_g , the viscosity is high ($\mu(T) = 4.7 \cdot 10^5 \text{ Pa} \cdot \text{s}$) and still no increase in contact line is visible.

We can conclude that the temperature inside the particles in the simulations is too low compared to the results from the experiment if we follow the same heating protocol. Hence it is clear that additional energy is required. Two possible methods to introduce this energy are (1) to increase the laser energy input or (2) to increase the initial particle temperature.

4.2.1 Increased laser power

The prescribed laser power of $P = 35 \text{ }\mu\text{W}$ ($P^{2D} = 0.695 \text{ W/m}$), which we call the ‘reference laser power’ P_{ref} from now on, appears to be too low to heat up the system enough for immediate flow. Therefore, we increased the laser power to see the effect on the sintering dynamics. The results for laser power $P = [10P_{\text{ref}}, 20P_{\text{ref}}, 30P_{\text{ref}}, 50P_{\text{ref}}]$ are shown in Figure 10, where the evolution of the contact line is shown in time. The set of experimental data points is shown as well. The dynamics of the contact line from the simulations give an S-shaped curve,

Figure 7: The evolution of the temperature in time, measured in the region of the liquid bridge, for experiments with particle radius $R = 60 \text{ } \mu\text{m}$, heating chamber temperature $T_\infty = 53 \text{ } ^\circ\text{C}$, pulse energy $E_p = 28 \text{ } \mu\text{J}$ and pulse duration $t_b = 0.8 \text{ s}$.

Figure 8: The evolution of the contact line in time for the simulations mimicing the sintering experiment, with experimental data points. All material and processing parameters are taken from Table 1. Note that the laser is switched on at time $t = 0 \text{ s}$ in both cases.

which is different from the experimental results that increase according to $L = c_1 - \exp(-c_2 t)$. None of the increased laser powers $P = [10P_{\text{ref}}, 20P_{\text{ref}}, 30P_{\text{ref}}, 50P_{\text{ref}}]$ allows the contact line to reach the same slope immediately around time $t = 0 \text{ s}$. Furthermore, only the simulation with $P = 10P_{\text{ref}}$ underestimates the final contact line, even though this laser power already exceeds the actual experimental value of approximately $4P_{\text{ref}}$. The other simulations show an overshoot in contact line with respect to the experiments.

Figure 9: The evolution of the contact line in time for the simulations mimicing the sintering experiment without heat losses, with experimental data points. All material and processing parameters are taken from Table 1. Instead of Eq. (17), $-k\nabla T \cdot \mathbf{n} = 0$ is used.

4.2.2 Increased initial temperature

Following the analysis of Hejmady et al. (2019a), the fit value of the viscosity is $\mu(T) = 143 \text{ Pa}\cdot\text{s}$ when fitting the experimental data on the isothermal modified Frenkel model (Frenkel (1945); Eshelby (1949); Pokluda et al. (1997)). This corresponds to a temperature of $T = 123.6^\circ\text{C}$ following Eq. (6). We performed an isothermal simulation at this temperature and the result of the evolution of the contact line in time is shown in Figure 11 together with the set of experimental data. The isothermal simulation follows the data points well up to time $t = 0.35 \text{ s}$. It seems that from this moment on the flow is prohibited by viscoelastic effects or the effect of the substrate.

Next, we performed simulations using the method and parameter values as described before (including the effect of the laser beam), but now with an increased initial temperature $T(t = 0) = 123.6^\circ\text{C}$. The result of the evolution of the contact line in time is shown in Figure 12 together with the experimental data. The heat loss seems to be too fast in the simulations with respect to the experiments. We can tune the heat loss by changing the convection coefficient. The result of the evolution of the contact line for the simulation with convection coefficient $h = 5 \text{ W}/(\text{m}^2 \cdot \text{K})$ is shown in Figure 13. Up to time $t = 0.35 \text{ s}$ the simulation follows the experimental data points well, but after this time the cooling down is too slow again. In Figure 14, the maximum temperature in the system is shown in time for the simulations presented in Figures 12 and 13. It seems that taking a constant convection

Figure 10: The evolution of the contact line in time for different values of the laser power $P = [10P_{\text{ref}}, 20P_{\text{ref}}, 30P_{\text{ref}}, 50P_{\text{ref}}]$, with experimental data points. All other material and processing parameters are taken from Table 1. The maximum temperature inside the system is given at $t = 0.8$ s for laser power $P = 10P_{\text{ref}}$ and at the contact line length of $L = 0.09$ mm for laser powers $P = [20P_{\text{ref}}, 30P_{\text{ref}}, 50P_{\text{ref}}]$.

Figure 11: The evolution of the contact line in time at temperature $T = 123.6^\circ\text{C}$ under isothermal conditions, with experimental datapoints.

coefficient h either overestimates or underestimates the heat loss in the system.

4.3 Viscoelastic material

One of the differences between the experiments and the simulations is the rheological material behavior. In the simulations, we used a viscous fluid model, whereas polystyrene behaves as a viscoelastic fluid. We implemented the multimode Maxwell model as presented in Hejmady

Figure 12: The evolution of the contact line in time with initial temperature $T(t = 0) = 123.6^\circ\text{C}$, with experimental datapoints. All other material and processing parameters are taken from Table 1 and laser power $P = P_{\text{ref}}$ is used.

Figure 13: The evolution of the contact line in time with initial temperature $T(t = 0) = 123.6^\circ\text{C}$ and convection coefficient $h = 5 \text{ W}/(\text{m}^2 \cdot \text{K})$, with experimental datapoints. All other material and processing parameters are taken from Table 1 and laser power $P = P_{\text{ref}}$ is used.

et al. (2019a). Instead of Eq. (3), we now solve

$$-\nabla \cdot (-p\mathbf{I} + 2\eta_s\mathbf{D} + \boldsymbol{\tau}) = \mathbf{0} \quad \text{in } \Omega, \quad (18)$$

with the viscoelastic extra-stress tensor $\boldsymbol{\tau}$ written in the conformation tensor form

$$\boldsymbol{\tau} = G(\mathbf{c} - \mathbf{I}), \quad (19)$$

Figure 14: The evolution of the maximum temperature in time with initial temperature $T(t = 0) = 123.6^\circ\text{C}$ for convection coefficients $h = 50 \text{ W}/(\text{m}^2 \cdot \text{K})$ and $h = 5 \text{ W}/(\text{m}^2 \cdot \text{K})$. All other material and processing parameters are taken from Table 1 and laser power $P = P_{\text{ref}}$ is used.

where $\eta_s = 1 \text{ mPa} \cdot \text{s}$ is the solvent viscosity, $G = \eta_p/\lambda(T)$ the modulus, η_p the polymer viscosity and $\lambda(T)$ the temperature-dependent relaxation time. The evolution of the conformation tensor $\mathbf{c}$ is for the multimode upper-convected Maxwell model

$$\lambda \overset{\nabla}{\mathbf{c}} + \mathbf{c} - \mathbf{I} = \mathbf{0}. \quad (20)$$

Herein, $\overset{\nabla}{(\cdot)} = D(\cdot)/Dt - (\nabla \mathbf{u})^T \cdot (\cdot) - (\cdot) \cdot \nabla \mathbf{u}$ denotes the upper-convected derivative. Similar to the temperature-dependent viscosity, we compute the relaxation time $\lambda(T)$ per mode using

$$\lambda(T) = \lambda_{\text{ref}} 10^{\left(\frac{-C_1(T - T_{\text{ref}})}{C_2 + (T - T_{\text{ref}})} \right)}. \quad (21)$$

Herein, λ_{ref} is the relaxation time at reference temperature T_{ref} and C_1 and C_2 are fitting parameters. For temperatures below the glass transition temperature T_g the relaxation time goes to infinity

$$\lambda(T < T_g) \rightarrow \infty. \quad (22)$$

Because the reference laser power P_{ref} is too low to show any flow, we use a laser power $P = 10P_{\text{ref}}$, which is approximately two times the actual experimental value. All other material and processing parameters are taken from Table 1. In Figure 15, the difference in evolution of the contact line between the viscous and viscoelastic response is shown, together

with the set of experimental data. Only a minor difference in sintering dynamics can be observed between the simulations with a viscous and viscoelastic fluid model. As is shown in Bailemans et al. (2017), the contact line of the viscoelastic fluid increases faster than the contact line of the viscous fluid **due to the elastic response of the polymer. This behavior is only visible if transient rheology is taken into account.** However, this cannot explain the difference in sintering behavior we observe between the experiments and simulations.

Figure 15: The evolution of the contact line in time for viscous and viscoelastic material properties with laser power $P = 10P_{\text{ref}}$, with experimental datapoints. All other material and processing parameters are taken from Table 1.

4.4 Substrate

To assess the effect of the substrate on the temperature distribution, we performed simulations solving only the energy balance Eq. (5), neglecting flow. We used two different geometries, as shown in Figure 16, to see the effect of contact area between the particles and the substrate. The substrate is modeled as a steel plate of 20×1 mm with density $\rho_s = 8000 \text{ kg/m}^3$, specific heat capacity $c_{p,s} = 0.5 \text{ kJ/(kg}\cdot\text{K)}$ and thermal conductivity $k_s = 50 \text{ W/(m}\cdot\text{K)}$. The geometry of the two distinct particles (referred to as ‘two’) is created by making a cut-through along the x -axis at $y = -0.98R$ of the original geometry as shown in Figure 3(a). The geometry of the elongated circle is created by connecting two circle halves with a rectangle and again making a cut-through along the x -axis at $y = -0.98R$ (referred to as ‘one’). The size of the connecting rectangle is chosen such that the areas of the two geometries are equal. At the outer boundary of the particle(s), the heat loss term given in Eq. (17) is prescribed. At the

interface between the particle(s) and the substrate, we couple the heat transfer by applying the constraint

$$[\nabla T \cdot \mathbf{n}]_{\text{particle(s)}} = [\nabla T \cdot \mathbf{n}]_{\text{substrate}}. \quad (23)$$

The laser beam only heats up the particle(s), i.e. the laser beam does not interact with the substrate. Furthermore, we neglect contact resistance due to air gaps or particle roughness. Therefore, we consider the upper limit of energy loss to the substrate.

Figure 16: Geometry of the particle(s) on the substrate (a) ‘two’ and (b) ‘one’.

Using the parameters and initial condition $T(t = 0) = T_\infty$ with laser power $P = P_{\text{ref}}$ as used in Hejmady et al. (summarized in Table 1), we find that the highest temperature is reached at time $t = 0.8\text{ s}$ for both systems. The maximum value of the temperature is $T = 54.8^\circ\text{C}$ for geometry ‘two’ with the two distinct particles, while the maximum value of the temperature is $T = 55.3^\circ\text{C}$ for geometry ‘one’ with the elongated circle. This temperature difference is caused by the different amounts of material in the area where the laser beam acts inside the system. However, the main conclusion is that the maximum value of the temperature is even lower than the one computed without substrate and no material is able to flow.

4.4.1 Increased initial temperature

Starting at an increased initial temperature $T(t = 0) = 123.6^\circ\text{C}$ for the powder particles, while keeping the initial temperature of the substrate at $T(t = 0) = T_\infty$, we find a temperature distribution of the particles as shown in Figure 17 for the two different geometries at times $t = 0.01\text{ s}$, $t = 0.1\text{ s}$ and $t = 1\text{ s}$. Within the first time step, the contact area between the particles and the substrate gets a value of $T = T_\infty$, which suggests that the polymer in contact with the substrate will remain solid. **This shows that the substrate acts as energy drain, due to the excessive conductive heat transfer from the warm small polymer particles to the cold large steel substrate.**

In Figure 18, we show the dynamics of the maximum temperature in time for the two different geometries and for two different values of the convection coefficient $h = 50\text{ W}/(\text{m}^2\cdot\text{K})$ and $h = 5\text{ W}/(\text{m}^2\cdot\text{K})$. All four results reach the glass transition temperature T_g between time $t = 0.14\text{ s}$ and $t = 0.18\text{ s}$. Again, the effect of the increased amount of material in the area where the laser beam acts inside the system causes the slightly slower decrease in temperature for geometry ‘one’ with respect to geometry ‘two’. In all of these cases, the value of the convection coefficient is of minor importance, because the substrate acts as an energy drain and dominates the heat loss dynamics. This is slightly different from the results of Großer et al. (2012) who found similar contributions of the heat loss into the air and the substrate. However, they consider smaller increases in temperature and assume that effect of the laser beam can be described as a surface source.

5 Conclusions

We compared numerical simulations of the sintering process of two polystyrene particles with experimental results. Using the parameters as presented in Hejmady et al. (2019a), the simulations show that no flow occurs, because the maximum temperature stays below the glass transition temperature T_g . Increasing the laser power P in the simulations gives different flow dynamics than observed in the experiments, i.e. the graph of the contact line in time is S-shaped in simulations, whereas the start of the S-shaped curve is not visible in

Figure 17: Close-up of the temperature distribution at times (a)-(b) $t = 0.01$ s, (c)-(d) $t = 0.1$ s and (e)-(f) $t = 1$ s for geometries ‘two’ and ‘one’ with initial temperature $T(t = 0) = 123.6^\circ\text{C}$ for the powder particles, keeping the initial temperature of the substrate at $T(t = 0) = T_\infty$. All other material and processing parameters are taken from Table 1 and laser power $P = P_{\text{ref}}$ is used. Note that effects of flow are neglected.

the experiments.

From isothermal calculations at $T = 123.6^\circ\text{C}$ we find a good agreement of the results with the experimental data up to time $t = 0.35$ s. At that point in time, the contact radius connecting the particles in the experiments stops increasing, which is probably due to effects from the substrate. Simulations including the effect of the laser beam and heat loss via convection and radiation but starting at the elevated temperature $T = 123.6^\circ\text{C}$ show that a convection coefficient $h = 50 \text{ W}/(\text{m}^2 \cdot \text{K})$ immediately overestimates the heat loss, whereas a convection coefficient $h = 5 \text{ W}/(\text{m}^2 \cdot \text{K})$ gives results that are close to the experimental values

Figure 18: The evolution of the maximum temperature in time with initial temperature $T(t = 0) = 123.6^{\circ}\text{C}$ for the different geometries and different convection coefficients $h = 50 \text{ W}/(\text{m}^2 \cdot \text{K})$ and $h = 5 \text{ W}/(\text{m}^2 \cdot \text{K})$. All other material and processing parameters are taken from Table 1 and laser power $P = P_{\text{ref}}$ is used. Note that effects of flow are neglected.

up to time $t = 0.35 \text{ s}$ and underestimates the heat loss from there.

Most of the simulations are performed using a viscous model describing the fluid dynamics, but the polymer material behaves according to a viscoelastic fluid. Therefore, we implemented the multimode Maxwell model as presented in Hejmady et al. (2019a). Due to the transient viscoelastic behavior, the increase in contact line is faster compared to that obtained with purely viscous models, as was concluded in Balemans et al. (2017). However, the difference in evolution of the contact line using viscous and viscoelastic rheological models is minor compared to the effects of thermal conditions in the system.

From the optical images of the sintering of the two particles in Hejmady et al. (2019a), it is clear that around time $t = 0.35 \text{ s}$ the liquid bridge between the particles touches the steel substrate. To study the thermal effect of the substrate, we solved the energy balance of powder particles on a substrate neglecting flow. We used a geometry of two circles that are barely connected to each other (‘two’) and a geometry of an elongated circle (‘one’) to see the effect of the contact area between the particles and the substrate. In both cases, the substrate acts as energy drain and the polymer close to the contact area immediately gets the same temperature value as the substrate. Although the heat loss towards the substrate is larger for geometry ‘one’, the total heat loss is less due to an increased amount of material in the area where the laser beam acts inside the system. Based on these results it is clear

that a polymer substrate is required in two-particle studies to mimic the actual laser sintering process.

We can conclude that knowledge of the temperature distribution of the system is key to correctly describe the sintering process of two polymer particles; viscoelasticity is of minor importance. A constant value for the convection coefficient h is insufficient to describe thermal effects in simulations without a substrate; a convection coefficient that depends on time and/or location might account for the effect of the substrate. It seems that we are missing some phenomena in our numerical simulations that occur in the experiments. Possible phenomena are softening of the material below the glass transition temperature T_g , a strongly localized heating zone at length scales that can not be resolved with the present IR imaging technique leading to partially liquefied particles or a non-uniform energy distribution over the time period of the laser pulse. For further steps it is essential to measure the temperature in the experiments in real-time with a much higher spatial and temporal resolution to gain detailed insight in the thermal impact of the laser beam and the following thermal behavior of the system. Unfortunately, these experimental capabilities are not available yet.

Acknowledgements

This work is part of the Additive Manufacturing program of the Brightlands Materials Center.

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