## Effect of processing conditions on crystallization kinetics during materials extrusion additive manufacturing

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Material extrusion additive manufacturing processes force molten polymer through a printer nozzle at high (> 100 s<sup>-1</sup>) wall shear rates prior to cooling and crystallization. These high shear rates can lead to flow-induced crystallization in common polymer processing techniques, but the magnitude and importance of this effect is unknown for additive manufacturing. A significant barrier to understanding this process is the lack of *in situ* measurement techniques to quantify crystallinity after polymer filament extrusion. To address this issue, we use a combination of infrared thermography and Raman spectroscopy to measure the temperature and percent crystallinity of extruded polycaprolactone during additive manufacturing. We quantify crystallinity as a function of time for the nozzle temperatures and filament feed rates accessible to the apparatus. Crystallization is shown to occur faster at higher shear rates and lower nozzle temperatures, which shows that processing conditions can have a dramatic effect on crystallization kinetics in additive manufacturing.

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#### Introduction

Material extrusion processes are widely used in additive manufacturing (AM) due to the affordability of the raw materials and a straightforward printing process. In filament-based materials extrusion, a solid filament is drawn into a printer nozzle, heated to a temperature where the polymer flows readily, then extruded layer-by-layer onto a build plate.[1] The polymer flow in the nozzle is characterized by shear rates of order 100 s<sup>-1</sup>,[2] which leads to significant chain stretch, orientation, and disentanglement in the melt prior to deposition on the build plate.[3, 4] After deposition, the extrudate layers weld and solidify to generate a desired product.

Depending on the polymer, the solidification process will either occur *via* a glass transition or crystallization, and the type of process will have a significant impact on the mechanism of strength enhancement of the weld between polymer layers. Glassy polymers form welds by polymer diffusion across the weld zone.[5] The polymer chain dynamics follow a Williams-Landel-Ferry relationship as the temperature approaches the glass transition,[6] which can be leveraged to determine an effective weld time during AM materials extrusion processes.[2] The weld strength for these glassy materials increases with the effective weld time  $\tau$  with a power-law dependence of  $\tau^{1/2}$  following the theory developed by Wool,[5] although the long-time weld strength of polymer layers from AM materials extrusion falls well below the fracture strength of the neat polymer.

Solidification by way of crystallization has received much less attention in AM materials extrusion processes, although we can gain insight from prior work on the welding and fracture of semicrystalline polymers. Studies on ultrahigh molecular weight polyethylene (UHMWPE) have shown that weld strength between interfaces follows the  $\tau^{1/2}$  dependence on the welding time when measuring fracture *above* the melting point.[7] In contrast, the weld strength of UHMWPE at room temperature is comparable to the strength of the semicrystalline bulk material regardless of welding time.[7] The high weld strength in the semicrystalline state is attributed to cocrystallization across the interface during crystal thickening below the melt temperature.[8] Conditions where cocrystallization is prohibited, such as when one of the interfaces is preannealed prior to contact, generate much weaker interfaces.[9]

An additional confounding issue is that the temperature and flow history can have a dramatic effect on polymer crystallization kinetics and semicrystalline morphology. Flow-induced crystallization can be observed using a variety of thermal and mechanical protocols.[10] Conditions where isothermal shear flow in the melt state was followed by rapid cooling are relevant to the AM materials extrusion process; for example, Eder *et al.* observed that a highly-oriented "skin layer" of semicrystalline material increased in thickness with increasing extrusion speed and slit-die length in extruded polypropylene.[11] Additional optical measurements in a slit-die showed that birefringent pre-crystalline material could be formed during shear.[10] The birefringent structures melted once shear flow was stopped, however the timescales for melting increased dramatically at temperatures near the spherulite melting temperature. Hamad *et al.* monitored polypropylene crystallization on a rheometer after different amounts of shear in the melt state prior to crystallization.[12] They observed that shear flow applied above the maximum reported equilibrium melt temperature (~210 °C)[13] had a diminishing effect on the crystallization kinetics compared with shear flow applied at temperatures as low as 160 °C.

Since AM materials extrusion is a layer-by-layer process, *in situ* knowledge of temperature and crystallinity of an extruded layer prior to the deposition of an additional layer is critical to understanding the welding process. Temperature measurements in the extrudate have been performed using both contact and non-contact methods. The primary contact-based thermal measurements have been performed using thermocouples embedded in the build plate of the printer.[14, 15] These measurements are limited to a single position in the extrudate, and the accuracy of thermocouple measurements depends on the contact between the thermocouple and the sample. More recently, infrared (IR) thermography was implemented as a non-contact temperature measurement in filament extrusion processes.[16, 17] IR thermography allows for temperature mapping over a region of the extrudate to measure the cooling rate in multiple printed layers in additive processes.[16]

Process line measurements of crystallinity in additive manufacturing are less frequently employed, although some results using X-ray scattering have been reported. X-ray diffraction measurements were performed on polycaprolactone (PCL) flowing through the nozzle of a custom-built material extruder.[18] The extended nozzle geometry allowed for diffraction measurements at different positions along the nozzle length, where the appearance and orientation of crystalline domains could be monitored. Offline small angle X-ray scattering (SAXS) measurements performed on material-extruded PCL indicated that crystalline orientation in the printing direction was increased at higher polymer feed rates and lower nozzle temperatures.[19] Although X-ray scattering measurements are successful in characterizing crystallinity, process line measurements using these techniques are limited to synchrotron sources. There is a clear measurement need for additional process line measurements of crystallinity in additive manufacturing.

Raman spectroscopy has shown great success in characterizing polymer crystallization in processing flows. Although Raman spectroscopy is not a direct measurement of crystallinity, relative peak intensities in the Raman spectrum can often be correlated with a percent crystallinity. Since Raman is an optical scattering phenomenon, the measurement can be performed in a

3

backscattering mode using fiber optic coupling to facilitate process line measurements. This operating mode has been used to measure crystallinity in polyolefins undergoing blown film extrusion[20] and fiber spinning processes.[21] In our prior work, we developed a linear relationship between the Raman spectrum of PCL and crystallinity.[22] Raman probe techniques should therefore be a viable in-line method for measuring crystallinity in material extrusion processes.

In this paper we use a combination of IR thermography and Raman spectroscopy to demonstrate the effect of material extrusion processing conditions on the crystallization kinetics of PCL. We isolate the effect of the extrusion and deposition process on polymer crystallization kinetics by continuous printing onto a belt conveyor system. This simplified setup removes any temperature or diffusion effects from extrudate layer-layer interactions and allows time-averaged measurements of Raman spectra and IR intensity as a function of distance or time from the extruder nozzle. By varying the nozzle temperature and flow rate, we can determine the conditions where the printing process enhances crystallization kinetics.

#### **Experimental**

The polycaprolactone used in these experiments was purchased in filament form (Flexible Filament, Makerbot) with a diameter of 1.75 mm and used as received (see Disclaimer). The molar mass distribution was measured using a Waters Breeze gel permeation chromatography system with differential refractive index detection. The system used three Waters Styragel HR columns: HR 4, HR3, and HR 0.5 as the stationary phase and the mobile phase eluent was tetrahydrofuran at 35 °C. The mass average molar mass of the polycaprolactone filament is 96.7 kg/mol with a dispersity of 1.73, which was determined based on a calibration curve of narrow dispersity polystyrene standards with peak-average molar masses ranging from 0.5 kg/mol to 400 kg/mol.

The filament is used in the experimental setup shown in Figure 1. A print head (High Temperature Cobra Extruder, Micron E.M.E) consisting of a drive wheel, heater, and nozzle is held stationary above a belt conveyor (HAAKE, Thermo Fisher Scientific). The length of the heated region is 10 mm. The temperature of the heater is set by a temperature controller (Watlow), and the rotation of the drive wheel is set using a DC motor driver (DRV 8834, Texas Instruments) controlled via Arduino. The nozzle has a diameter of 0.5 mm and is fixed at a height 2 mm above the conveyor belt. The belt velocity is controlled so that the extrudate exiting the nozzle does not coil on the belt or visibly draw from the nozzle. The conveyor belt exhibited a strong Raman spectrum in the spectral region of interest, so a replacement belt was fashioned from a polyethylene-coated duct tape. During operation, a single extruded layer travels on the belt from the nozzle to a take-up wheel. Steady-state printing conditions were chosen such that continuous extrusion was possible. Filament feed rates were measured by marking the filament at 10 cm increments and measuring the rate at which the markings were drawn into the print head. Accessible feed rates were between 0.18 cm/s at nozzle temperature of 90 °C and 0.31 cm/s at 140 °C.



Figure 1. Schematic diagram of experimental setup for process line Raman spectroscopy.

A Raman fiber optic probe (InPhotonics) was positioned above the filament to perform Raman spectra measurements. The fiber probe is connected via two fiber optic cables to a DXR Raman microscope (ThermoFisher) using a 780 nm excitation laser operating at 24 mW. A lens at the end of the Raman probe focuses the laser light onto a nominal spot size of 105  $\mu$ m, and the backscattered light is collected and returned to the spectrometer for analysis. The exposure time for Raman measurements was 15 s, and eight exposures were averaged together to generate the recorded Raman spectrum. The Raman spectra in the carbonyl (C=O) stretch region of the spectrum are analyzed to determine crystallinity using a method developed previously.[22] Briefly, we fit the experimental spectra to a set of three basis spectra that account for chains in an amorphous conformation, chain-chain dipole interactions, and chains ordering in a crystalline lattice. The integrated intensity of the crystalline basis spectrum normalized by the total integrated intensity of the C=O stretch region is directly proportional to the crystallinity as measured by DSC.[23] We calculate the mass fraction crystallinity  $\alpha_c$  from each Raman spectrum as

$$\alpha_{\rm c} = \beta \frac{I_{\rm c}}{I_{\rm tot}} \tag{1}$$

where  $I_c$  is the integrated intensity of the crystalline basis spectrum and  $I_{tot}$  is the integrated intensity of the entire C=O stretch region. The coefficient  $\beta = 1.26$  was determined by measuring the Raman spectrum of different PCL samples with crystallinities measured via DSC.

IR thermography measurements were performed by replacing the fiber optic probe with an IR camera (A6700sc, FLIR). Videos of the extrudate were recorded at various positions along the conveyor belt at a frame rate of 60 Hz and an integration time of 2.4 ms – example images from the videos are shown in the Supplementary Material. The IR photon count at the center of the extrudate was recorded over a period of five seconds. Additional IR videos were also taken of the extrudate emerging directly from the nozzle with the belt conveyor removed. The total IR photon

count was converted to temperature via calibration measurements of the IR photon count of PCL samples placed on a temperature-controlled stage (THMS600, Linkam Scientific). The total count versus temperature is well fit using a general form of Planck's equation as shown in the Supplementary Material.

Melt viscosity measurements of the PCL filament material were performed on a rheo-Raman microscope. Rheology measurements were performed using a 20 mm cone and plate geometry with cone angle 1° and a truncation gap of 52 µm. Reflection-mode optical imaging through the base of the rheometer was performed using crossed polarizers to confirm that no birefringent (crystalline) structure appeared below the equilibrium melt temperature on the timescale of the viscosity measurement.

#### **Results and Discussion**

To examine the effect of flow in the nozzle on the crystallization kinetics, we must first characterize the viscosity of PCL in the melt state. The viscosity of the PCL filament material is shown in Figure 2, where the data has been shifted to 100 °C using time-temperature superposition. Although the viscosity measurements at 60 °C are measured below the equilibrium melting temperature of PCL, we did not optically observe the growth of semicrystalline domains during the viscosity measurement. The polymer has a constant viscosity near 2000 Pa s at lower shear rates and exhibits noticeable shear thinning as the shear rate increases. The viscosity follows the Carreau model with a negligible high shear viscosity,

$$\eta = \eta_0 \left[ 1 + \left( \lambda \dot{\gamma} \right)^2 \right]^{(n-1)/2} , \qquad (2)$$

which includes the zero-shear viscosity  $\eta_0$ , time constant  $\lambda$ , and the power law index *n*. The best-fit values of eq 2 to the data result in  $\eta_0 = 2008 \pm 9$  Pa·s,  $\lambda = 0.065 \pm 0.014$  s, and  $n = 0.75 \pm 0.04$ .



Figure 2. Viscosity versus shear rate for PCL at three temperatures. The line shows the best fit of eq 2.

To determine the nozzle shear rate based on the filament feed rates, we can model the printing process as extrusion through a capillary die. The feed rate and nozzle temperature can then be used to determine the shear rate in the nozzle. The nozzle geometry consists of a circular capillary of radius  $R = 250 \ \mu\text{m}$  and length  $L = 800 \ \mu\text{m}$  just prior to extrusion onto the conveyor belt. Although we note that the ratio L/R = 3.2 is most likely dominated by entrance effects,[24] we will assume that steady-state flow occurs over the length of the capillary. The wall shear rate  $\dot{\gamma}_W$  for a power law fluid in a circular capillary is

$$\dot{\gamma}_{\rm W} = \frac{Q}{\pi R^3} \left( 3 + \frac{1}{n} \right) \tag{3}$$

where Q is the volumetric flow rate of the PCL melt and n is the power law index. The volumetric flow rate can be determined by a mass balance between the solid filament mass flow rate and the mass flow rate in the capillary. Since the mass flow rate is the product of the density  $\rho$  and the volumetric flow rate Q, we write the mass balance as

$$\rho_s Q_s = \rho_e Q_e \ . \tag{4}$$

The subscript "s" indicates properties of the solid filament, and "e" indicates properties of the melt in the nozzle. The density of the solid filament is 1100 kg/m<sup>3</sup>, and the filament volumetric flow rate for the filament of radius  $R_s = 0.9$  mm is the product of the filament feed rate f and the cross-sectional area,  $Q_s = \pi R_s^2 f$ . The density of the extrudate is calculated from an empirical relationship for the specific volume  $v_e = 1/\rho_e$  as

$$v_e = v_0 e^{\varepsilon T} \tag{5}$$

where the fit parameters are  $v_0 = 0.9049 \text{ cm}^3/\text{g}$  and  $\varepsilon = 6.392 \times 10^{-4} \text{ K}^{-1}$ .[25] The temperature *T* is set equal to the nozzle temperature. To confirm that the extrudate was being heated to the nozzle temperature we performed thermography measurements of the extrudate approximately 150 µm from the nozzle with the belt conveyor removed. The measured temperatures are (89.8 ± 1.0) °C, (104.2 ± 1.0) °C, and (133.3 ± 1.2) °C for the set temperatures of 90 °C, 110 °C, and 140 °C respectively. The temperature is independent of the nozzle feed rate to within measurement uncertainty.

The Raman spectrum of the PCL extrudate at different positions along the conveyor belt is shown in Figure 3 for a feed rate of 0.19 cm/s ( $\dot{\gamma}_{\rm W} = 450 \, {\rm s}^{-1}$ ) and a nozzle temperature of 110 °C.

The extrudate spectrum at short distances from the nozzle is characterized by a broad peak consistent with polycaprolactone in the melt state. As the extrudate moves away from the nozzle, the peak position in the C=O stretch band shifts from approximately 1730 cm<sup>-1</sup> to 1724 cm<sup>-1</sup> as the polymer crystallizes. The experimental spectra are well-fit by the three basis spectra, as indicated by the negligible residuals beneath each spectrum. At short distances from the nozzle the spectrum is comprised of the dipole-dipole and amorphous basis spectra, with a negligible contribution from the crystalline basis spectrum. The crystalline spectrum increases in intensity further from the nozzle, with a corresponding decrease in intensity of the amorphous component. The nominal Raman spot size is smaller than the nozzle diameter, and we therefore expect that the Raman measurement is probing the average chain conformations within a sampling volume that extends approximately 100  $\mu$ m into the extrudate surface.



**Figure 3**. Raman spectra of polycaprolactone extrudate and the basis spectra fits at the indicated distances from the extruder nozzle. The colored filled points indicate the raw data, the black line indicates the total fit, the blue line indicates the crystalline basis spectrum, and the grey lines indicate the dipole-dipole and amorphous basis spectra for each measurement. The colored open points beneath each spectrum indicate the residual for each fit. All spectra are normalized by the total integrated intensity in the C=O stretch region.

From the basis spectra we determine the crystallinity as a function of position as shown in Figure 4a for a representative set of filament feed rates at a nozzle temperature of 110 °C. At positions near the nozzle, the measured crystallinity is within the noise limit of 0.025 mass fraction crystallinity. The crystallinity increases as the extrudate moves approximately 20 cm from the nozzle and continues to increase until the extrudate reaches the end of the conveyor at 45 cm. Crystallization continues as the extrudate is drawn onto the uptake wheel, and Raman-based crystallinity measurements on the extrudate 24 hours after printing indicate crystallinities in the range of 0.48 to 0.52. These final crystallinity values are near the room temperature crystallinity of 0.55 for a PCL of comparable molecular weight.[22] The temperature from IR thermography is shown in Figure 4b, which shows a rapid cooling of the extrudate at short distances from the nozzle. At distances beyond 16 cm the IR contrast between the extrudate and the background is negligible, and we do not report the temperature.



**Figure 4**. a) Crystallinity of PCL extrudate as a function of distance for the printer operating at 110 °C and different feed rates covering a wall shear rate range of (450 to 550) s<sup>-1</sup>. b) Temperature of the extrudate. The gray shaded region indicates crystallinities that are within measurement noise. The error bars indicate the standard deviation of measurements at each position.

The primary temperature loss from the extrudate is via convection at the polymer-air interface, which could potentially cause a temperature gradient in a cross-section of the extrudate. We can estimate the magnitude of the temperature gradient by determining the thermal resistance of the extrudate relative to the thermal resistance of the surrounding air via the Biot number Bi = hl/k, where *h* is the heat transfer coefficient at the polymer-air interface, *l* is a characteristic dimension of the extrudate cross-section, and *k* is the thermal conductivity of the polymer. Assuming free convection in air  $h = 20 \text{ W/(m}^2 \cdot \text{K})$ ,[26] a length scale equal to the radius of the

nozzle  $l = 250 \,\mu\text{m}$ , and a thermal conductivity  $k = 0.2 \,\text{W/(m \cdot K)}[27]$  yields Bi = 0.03, which in small enough to assume a negligible temperature gradient within the extrudate cross-section. The temperature measured at the surface of the extrudate from IR thermography is therefore a reliable indication of the temperature within the extrudate.

The results as a function of distance in Figure 4 can be converted to functions of time by dividing the distance by the belt speed for each feed rate, as shown in Figure 5. The resulting crystallization dynamics in Figure 4a show an almost negligible effect of the filament feed rate on crystallization kinetics, with the slowest feed rate crystallizing slightly slower. The temperature profiles in Figure 5b collapse onto a single curve. This is not unexpected, since the feed rate should have a negligible effect on the extrudate cooling rate. A significant rise in the crystallinity occurs approximately 20 s after extrusion, at which point the extrudate has cooled to temperatures below 40 °C. Measurements for printing conditions at 90 °C and 140 °C are included in the Supplementary Material; thermography measurements at 90 °C are not shown due to lack of IR contrast (i.e., low temperatures) at a distance 2 cm from the nozzle.



**Figure 5**. The data from Figure 3 plotted as a function of time for a) crystallinity and b) temperature. The gray shaded region indicates crystallinities that are within measurement noise. The error bars indicate the standard deviation of four measurements at each time.

We can now examine the effect of the wall shear rate on crystallization kinetics for the results shown in Figure 5a, as well as printing conditions at additional temperatures and wall shear rates. Figure 6 shows the time  $\tau_{01}$  at which the crystallinity exceeds a mass fraction of 0.1 as a function of the calculated wall shear rate for these conditions. Higher wall shear rates are accessible at higher nozzle temperatures due to the lower viscosity and lower density of the material being forced through the nozzle. Higher wall shear rates enhance the crystallization kinetics at lower nozzle temperatures, and the effect of shear is much less pronounced when extruding at higher nozzle temperatures. We note that all conditions are performed at nozzle temperatures above the equilibrium melting temperature of PCL (approximately 70 °C).



**Figure 6.** Crystallization time as a function of the estimated wall shear rate for three nozzle set temperatures.

Filament melting in the printer nozzle is a transient process; therefore, the temperature history of the filament is critical to understanding whether the faster crystallization kinetics are due to flow-induced crystallization or incomplete melting of the semicrystalline domains prior to extrusion. Although we cannot perform thermography measurements inside the nozzle, our IR measurements at the nozzle show that the extrudate is emerging at temperatures where PCL is expected to be in the melt state.[28] However, this is not sufficient to say that all crystalline material has melted by the time the polymer exits the extruder nozzle. The presence of crystallization kinetics at lower temperatures.[28] We also note that the flow and temperature history of the polymer in the nozzle is not well-understood; recent measurements of the deformation and temperature profiles in a printer nozzle have shown that the materials extrusion process is highly non-isothermal in the print head.[29]

In addition to incomplete melting, flow-induced crystallization could also explain the faster crystallization kinetics. Our results are in qualitative agreement with flow-induced crystallization measurements that impose shear in the melt state prior to a temperature quench – the effects of shear are more pronounced when flow is applied near the melting temperature. Any structures generated in flow are also expected to have long lifetimes above the equilibrium melting temperature compared to semicrystalline domains grown in isothermal conditions.[10] The rapid cooling of the extrudate outside the printer nozzle further prolongs the presence of flow-induced structures until the polymer reaches a temperature for spontaneous crystallization, at which point the remaining pre-crystalline structures act as nucleation sites. The high shear rates have a significantly reduced effect on crystallization kinetics at higher nozzle temperatures. We note our nozzle temperatures are significantly above the equilibrium melting temperature as measured from the intersection of the crystallization temperature and melting temperature (70 °C);[30] however, Strobl and co-workers have proposed that the equilibrium melting temperature should be significantly higher.[31] They argued from the Gibbs-Thompson rule that the equilibrium melting temperature should be determined from the linear relationship between the melting temperature and the inverse lamellar thickness extrapolated to zero inverse thickness (i.e., infinitely thick lamellae). Their SAXS measurements yielded an equilibrium melting temperature of approximately 99 °C. Our measurements indicate that shear flow at temperatures below the melting temperature of infinitely thick lamellae strongly enhance crystallization kinetics in filament-extrusion type processing flows.

From a molecular viewpoint, significant chain orientation and stretch is expected near the walls of the printer nozzle,[3] which will promote crystallization near the outer surface of the extrudate.[32] This outer shell of semicrystalline material would inhibit the diffusion of polymer

16

chains across the weld during the printing process. Since the Raman fiber optic probe is focused that the optically scattering semicrystalline domains in the extrudate will limit the Raman scattering volume to regions near the polymer-air interface.[33] This would make Raman sensitive to those crystalline surface layers that would have the largest effect on weld strength.

In addition to shear flow, we expect significant extensional flow as the polymer melt enters the constricted region of the nozzle.[34] Extensional deformation would be highest near the center of the extrudate and would lead to additional chain stretch, alignment, and disentanglement, which would further increase the rate of crystallization.

#### Conclusions

Incorporation of in-line Raman spectroscopy measurements in a simplified filamentextrusion additive manufacturing process allows us to characterize polycaprolactone crystallization kinetics as a function of the two control parameters: nozzle temperature and filament feed rate. By extruding onto a belt conveyor system with measured belt velocity we can easily measure crystallinity as a function of time following extrusion from the nozzle. Our results indicate that the processing conditions have a significant effect on crystallization kinetics when printing at lower temperatures in the melt state. Complementary IR thermography measurements indicate rapid cooling of the extrudate outside the nozzle with a cooling rate that is independent of the filament feed rate. This work immediately motivates further theoretical and computational demonstration of the conditions for complete melting in the print head and flow-induced crystallization due to polymer deformation during materials extrusion to determine the underlying mechanism for enhanced crystallization kinetics. Additional experimental work is necessary to determine the effect of printing conditions on semicrystalline domain orientation and chain alignment under conditions where flow-induced crystallization is expected. These results are critical to the understanding of process-property relationships in the additive manufacturing of semicrystalline polymers.

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### Supplementary Material for

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**Figure S1**. False color infrared thermography images of polycaprolactone extruded at a nozzle temperature of 140 °C and a feed rate of 0.30 cm/s taken at three distances from the nozzle: a) 2.8 cm, b) 7.6 cm, and c) 16 cm. The color scale on the right indicates the corresponding IR photon count (dimensionless). Extrudate motion is from top to bottom in each image.



**Figure S2.** Calibration of IR photon count versus temperature of a PCL sample on a hot plate. The symbols indicate measurements and error bars indicate the standard deviation of 10 measurements. The line shows the best fit to a general Planck equation:  $IR = A(\exp(B/T)-1)^{-1} + C$ , where *IR* is the IR photon count, *T* is the temperature, and *A*, *B*, and *C* are fitting parameters. The coefficients are  $A = (2.940 \pm 0.049) \times 10^7$ ,  $B = (3546.6 \pm 7.4)$  K, and  $C = 4691.0 \pm 5.6$ 





Figure S3. Temperature profiles of the PCL extrudate at 140 °C.