Polymer 154 (2018) 182–187

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

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

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HIGHLIGHTS

- Process line Raman spectroscopy and IR thermography during materials extrusion.
- Raman spectra provide non-destructive measure of % crystallinity.
- Crystallization rates are faster at lower temperatures and higher feed rates.

ABSTRACT

Material extrusion additive manufacturing processes force molten polymer through a printer nozzle at high (> 100 s^{-1}) 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.

1. 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^{-1} [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 τ 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

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https://doi.org/10.1016/j.polymer.2018.09.018
Received 7 June 2018; Received in revised form 29 August 2018; Accepted 9 September 2018
Available online 10 September 2018
0032-3861/ Published by Elsevier Ltd.

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 precrystalline 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 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.

2. 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 Fig. 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.

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 μm, and the backscattered light is collected and returned to the spectrometer for analysis. The exposure time for

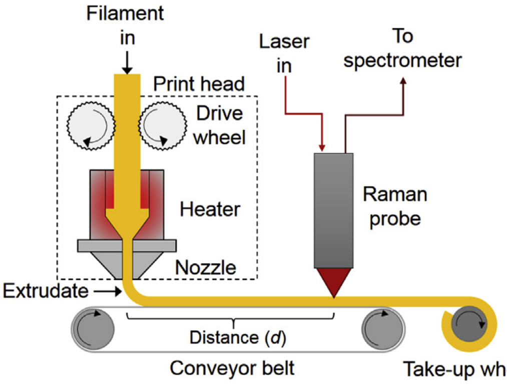

Fig. 1. Schematic diagram of experimental setup for process line Raman spectroscopy.

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