

Study on Inhibition Mechanism of Polymer Parts in Selective Inhibition Sintering Process

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Abstract

The selective inhibition sintering (SIS) process is an additive manufacturing technique that builds parts based on powder sintering. In this process parts are made upon deposition of a solution, called inhibitor, at the boundary profile. The inhibitor prevents polymer particles to coalescence under heat exposure on each layer. The inhibited boundary profile acts as a sacrificial mold that can be easily removed, leaving a chemically pure part. One of the influential factors in fabrication resolution by SIS is the proper selection of an inhibitor. The best inhibition mechanism results in ease of separation of the part from undesired regions while maintaining part accuracy. In this paper, we investigate a framework for selecting an appropriate inhibitor for the process. Different experiments have been performed and inhibition theory has been studied on polyamide (PA) samples. Specifically, as an alternative to exhaustive experiments on solutions and polymers, a hybrid method based on crystallization is proposed to characterize the effectiveness of the inhibitor. Differential Scanning Calorimetry (DSC) tests are used to study changes in thermal properties of the samples. It is found that the sintering period increases as crystallinity of the polymer decreases. Results show that polymer samples exposed to sodium hypochlorite solution has longer sintering periods. Design of experiments has been used to study shrinkage behavior of polymer samples through bulk sintering.

Introduction

Additive Manufacturing (AM) or 3D printing has enjoyed a recent surge of attention over the past decade. AM is the process of fabricating three-dimensional physical objects from digital models by additively combining material layers to form the final shape. Intensive research efforts have been primarily focused on the accuracy of parts fabricated through AM technologies such as Stereolithography (SLA), Selective Laser Sintering (SLS), Fused Deposition Modeling (FDM), Three-dimensional printing (3DP), etc., in order to monitor quality issues. Selective Inhibition Sintering (SIS) process is another AM technique through which parts are fabricated based on powder sintering. In this process, a solution is printed on each layer using a commercial inkjet printer at the boundary profile. Solution works as an agent which prevents powder particles to fuse at treated sections. There are three main consecutive steps in making parts by SIS: (I) Powder is uniformly spread on the build tank, (II) Solution is deposited on the boundary profile on each layer based on 2D cross sections of the 3D model, (III) A heater is moved along the x axis and the layer is sintered except boundary profiles. Back to step1, a new layer of powder is spread on the previous layer and the procedure is repeated (Figure 1). Finally, sintered and un-sintered regions are separated at the boundary. Variety of materials has been used in this process including ceramic, metal, and polymers [1-3].

Polymer sintering has wide variety of industrial applications such as in rotational moldings, dispersion coatings, and cold compression [4, 5]. This phenomenon occurs as a result of coalescence between solid powder particles under surface tension. For semi-crystalline materials, this formation often happens at a temperature above the glass transition temperature (T_g) and below the melting temperature (T_m) of the polymer. There are several parameters that affect polymer sintering including molecular weight, viscoelasticity, particle size (density), pore size, and particle geometry. In 1945, Frenkel developed the first model to capture sintering by studying the rate of coalescence resulted by viscous flow between two similar spherical particles [6]. Bellehumeur et al. [7] also studied the impact of particle geometry on resin polymer sintering by studying pairs of particles in a hot microscopy setup. He concluded that the impact of part geometry on sintering rate is not significant. It was also observed that viscosity of the resin influence the sintering rate such that lowering viscosity results in higher sintering rate. Barnetson et al. [8] studied sintering behavior of high molecular weight polyethylene (UHMWPE) under hot-air-circulating oven to derive the optimum temperature and time. In this research effort, similar molecular weight samples having different particles sizes were tested. Difference in particle size, density of the samples affects the sintering rate. The significance of porosity percentage and pore radius on sintering rate was obtained by examining the test cases.

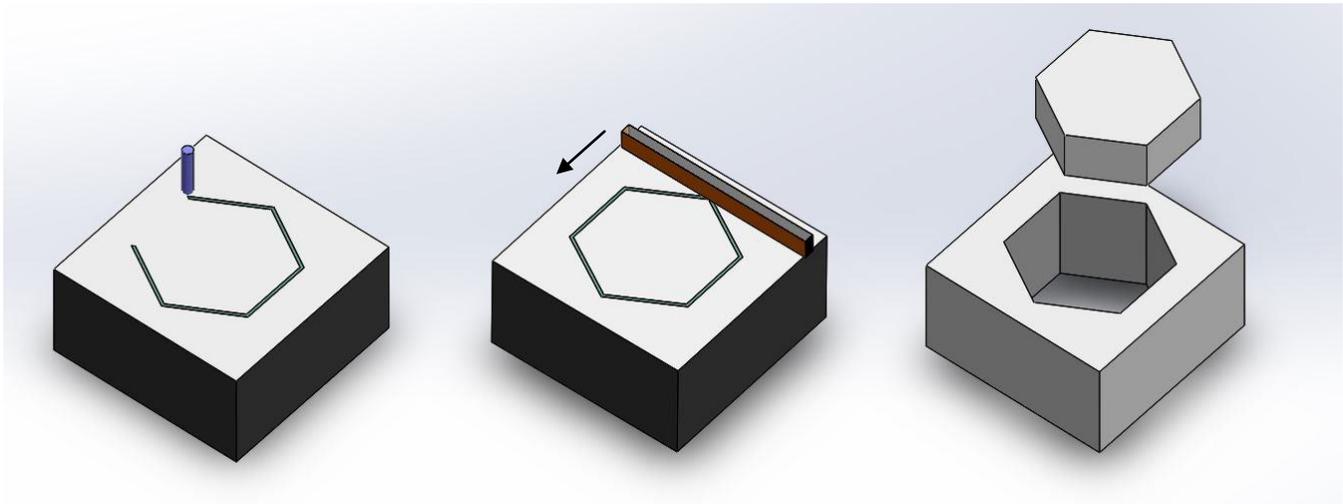


Figure 1. Selective Inhibition Sintering (SIS) process

It is vital to study sintering mechanism and the involved factors in SIS process. In previous research efforts, Asiabanpour et al. performed several experiments with various powders and inhibitors to derive parts with higher surface qualities. Inhibitors were examined on Polystyrene powder and Potassium Iodide (KI) solution was found to be a suitable inhibitor. However, this research was concentrated on limited number of polymers and solutions. Finding appropriate inhibitors to enable using variety of polymer powders and produce wide class of polymer products by SIS is still a challenge. This research study attempts to improve the inhibition mechanism of SIS by proposing an alternative method to explore inhibition efficiency based on degree of crystallinity of the polymer. Following section contains our proposed methodology. In section 3, our experimental investigation on inhibition mechanism is presented, and last two sections include conclusion and future research directions.

Methodology

We aim to investigate the applicability of using degree of crystallinity as a heuristic for selection of inhibitor. To choose an appropriate inhibitor, several factors are taken into account including molar mass,

viscosity, decomposition temperature, density, instantaneous chemical reaction of inhibitor with polymer powder and its stability to the end of the sintering process. Table 1 shows material properties of the candidate solution and Potassium Iodide. We focused our effort on a hypochlorite solution due to its molecular structure and its probable reaction with amide bonds of PA [9]. In selecting the solution, degradation of polymer chains is favorable. By degrading polymer chains and breaking them into shorter segments, the overall entanglements would significantly decrease and this would retard the sintering process (Figure 2). It is worthwhile to note that the sole breaking of chains may not be favorable, since it might increase the overall interaction between chains by increasing the number of chain end points. However, our results show that shorter chain segments result in retardation of the sintering process.

Table 1. Properties of inhibitor

Properties	Inhibitors	
Solution	Sodium Hypochlorite	Potassium Iodide
Formula	NaOCl (14.5% chlorine)	KI
Molar mass	74.44 gmol ⁻¹	166.028 gmol ⁻¹
Solubility in water	29.3 g (100 g) ⁻¹ (0 °C)	135 g (100 g) ⁻¹ (20 °C)
Viscosity	2.6 cp at 20 °C	1.0227 cp
Hazardous	2	1
Instability/reactivity	Normally stable	Normally stable
Density	1.23 gcm ⁻³	3.123 gcm ⁻³
Flammability	0	0

Influential factors in degradation of polyamides can be roughly categorized into three main pillars; (I) alteration in amount of water or organic liquids in the bonds, (II) change in degree of crystallinity; i.e. change in hydrogen-carbon packing, and (III) breakage of polymer molecules at C-N bond which leads to creating smaller molecules having the same chemical structure [10-12]. In order to detect the impact of the solution on the inhibition and have a better understanding of the change in crystallinity of polymer, three different solutions were selected and tested; 100% Sodium hypochlorite(NaOCl) solution (12% available chlorine), 60 % NaOCl mixed with 40% organic surfactant (2-Butoxyethanol), and 100% organic surfactant. The first solution was selected to achieve maximum concentration of solution mixed with polymer sample. Due to NaOCl's high surface tension, mixing was obtained by vigorous stirring until particles were completely exposed to the solution. The second solution contains 60% of the first solution with 40% of an organic surfactant added to achieve higher surface tension. This ratio was obtained by running several droplet tests using pipette on uniformly spread powder bed and monitoring penetration rates. The optimal penetration rate happens when there is spontaneous absorption into the substrate and the droplet does not spread after the initial impact. The third solution which is used as a reference sample helps us distinguish the impact of chemical reaction of NaOCl on polyamide samples. Pure surfactant solution is expected to slightly change polymer's thermal behavior while NaOCl is expected to significantly affect polymer's crystallinity by degrading polymer chains.

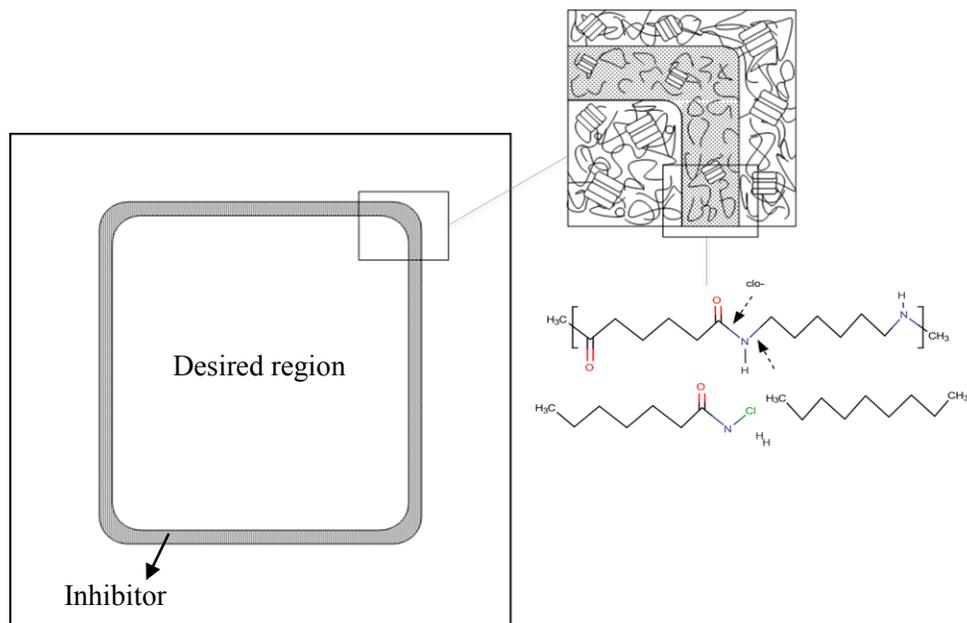


Figure 2. Probable reaction of hypochlorite solution with amide segments

DSC (Differential Scanning Calorimetry) measurements were used in order to compare solidification behavior of samples. DSC technique determines the heat flow that goes into or out of the material as a function of temperature (time). Polymer crystallinity (%), melt onset temperature (°C), melt peak temperature (°C), enthalpy (Jg⁻¹) can be calculated by quantifying the heat associated with the melting of the polymer powder. In this research study, PA samples dissolved in different chemical solutions were examined by DSC through the range of 0 °C to 120 °C. This modulated thermal treatment involved two main runs; heating at 1 °C per minutes up to the temperature of 40 °C, and heating at 3 °C per minutes to 140 °C. The heating treatment has been kept the same for all of the samples. Figure 3 shows sample heat flow behavior of original Polyamide sample.

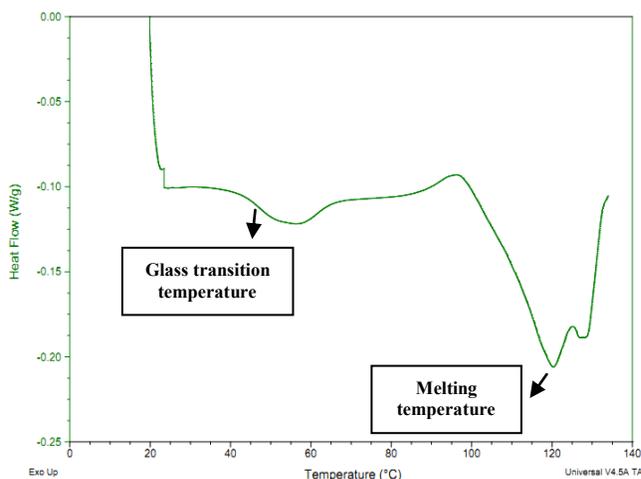


Figure 3. DSC graph of original PA sample (Left), Differential Scanning Calorimetry (Right)

PA samples were dissolved and exposed to the solutions overnight at 298 k. The data shown in Table 2 demonstrates the thermal properties of PA samples after exposure to the solutions. It reveals that changes in polymer crystallinity are distinct. The melt peak temperature of the pure NaOCl sample has decreased significantly compared to original PA.

There are several studies dedicated to applying hypochlorite solution to the membrane flux and examining polymer's degradation [13, 14]. The efficiency of PA degradation highly depends on PH and chlorine concentration in the solution. Therefore, higher concentration of active chlorine is likely to cause higher degradation and lower degree of crystallinity of the samples. Figure 4 exhibits an overlay of the heat flow of the treated samples.

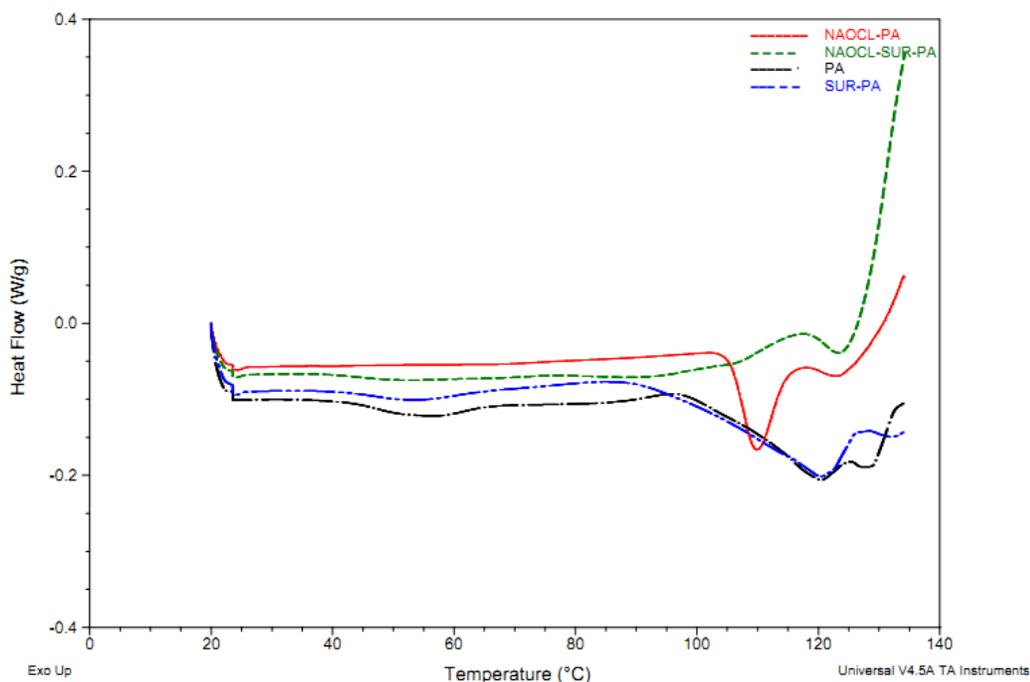


Figure 4. DSC graphs of PA under different processes

Table 2. Thermal properties of the samples

Sample	Tg	Melt onset temperature	Melt peak temperature	Enthalpy (Jg ⁻¹)
PA	46.83	120.29	120.35	40.24
PA- Surfactant	47.64	120.23	120.27	22.83
PA- Surfactant-NaOCl	45.67	124.33	123.26	14.37
PA- NaOCl	41.84	109.86	109.86	11.79

Crystallinity is calculated by integrating the areas (J/g) under peaks. Based on polymer's thermal history, melting peaks differ. The percent crystallinity can be derived using $(\Delta H_m - \Delta H_c)/\Delta H_m^\circ * 100$ [15] in which the nominator is obtained by finding the area J/g (enthalpy) under peaks of heating melt (ΔH_m) and cold crystallization (ΔH_c). ΔH_m° is a reference point and is representative of heat of melting for 100% crystalline polymer. For each polymer type, there is a commonly used reference point. In order to figure out the functional groups of our polyamide, Fourier Transform Infrared Spectroscopy with an ATR unit (ATR-FTIR) was employed. FTIR is a reliable technique that is widely applied to characterize and quantify different substances, specifically polymers. The principle of this method is based on capturing and measuring changes that occur in an internally reflected infrared beam as the beam is exposed to the sample.

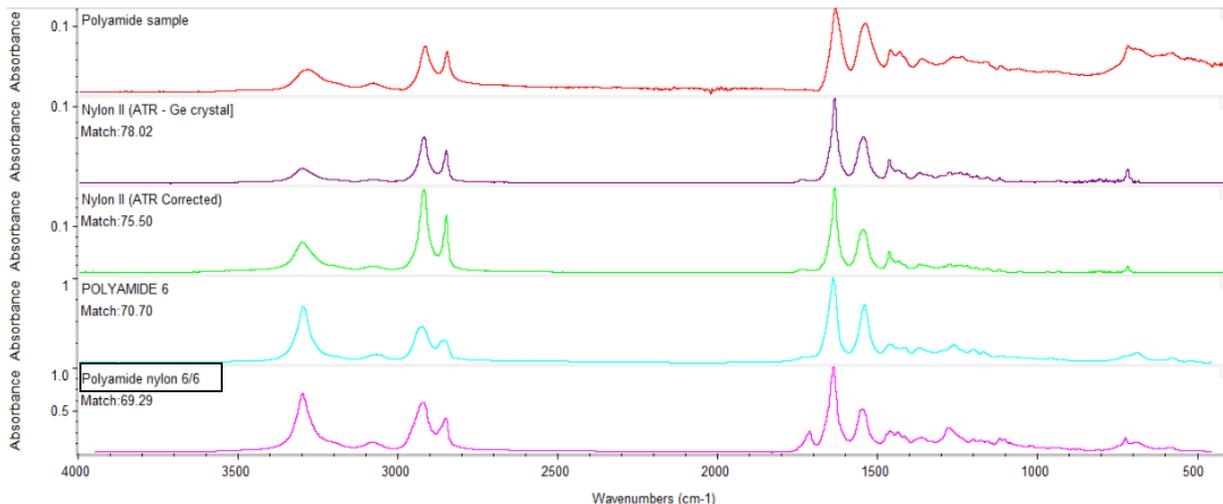


Figure 5. ATR-FTIR of polyamide sample to characterize the functional groups

IR spectra of the original PA were recorded in the range of 500-4000 cm^{-1} at the room temperature. Figure 5 demonstrates polymer sample's absorbance rate along with sorted similar groups. As it is shown, the observed rate is similar to what is obtained by nylon 6, 6. Therefore, in our calculations, we have deployed the reference heating of melting commonly used for nylon 6, 6 [16] as ΔHm° , which is 255.8 Jg^{-1} .

Experimental Study

In order to test inhibition efficiency of the selected solutions, several experiments were performed. A ceramic block made of Silica-alumina $(\text{AlO})_2 \text{SiO}_3$ was used as a power-bed during the sintering process. Alumina block is appropriate for our purpose since it is highly stable, obtains high melting temperature and has porosity of less than 3%. Moreover, it is observed that the temperature variation of ceramic powder bed is lower than wood and other types. Sintering is carried out using a heater source that moves across a horizontal line and has been designed to generate uniform heat distribution up to 80 $^\circ\text{C}$ on the powder bed. Each time, thin layer of polymer powder with the thickness of 0.1mm is spread on the ceramic block and exposed to heat until powder particles are solidified. This process is a good representative of SIS process since the same procedure happens during fabrication of polymer parts. The required sintering period differs depending on the speed of the heater, distance between part bed and the heater and the layer thickness of the polymer powder. The required sintering period is completed at the point which all polymer particles are joined together and solidified. PA powder was exposed to the solutions, and its performance was tested after thoroughly dried. For the first run of experiments, equal amount of each sample was uniformly spread on the same block and sintering periods were recorded under similar heating condition. Second run of experiments included bulk sintering of samples in the furnace with a defined heating ramp and final temperature which were experimentally obtained. Equal amounts of polymer samples were uniformly distributed on an aluminum block and heated with the rate of 10 $^\circ\text{C min}^{-1}$, starting at the room temperature (30 $^\circ\text{C}$) and heated up to 125 $^\circ\text{C}$. Inhibition efficiency of the solutions could be monitored by examining sintering percentage of the polymer blocks.

Design of Experiments

Design of experiments is to study influential factors in material shrinkage of polymer through sintering process. The main objective is to minimize average shrinkage along X and Y axes. One of the factors that limit the bulk sintering for SIS process is the uncontrollable shrinkage of material that occurs during heating. It is challenging to find the temperature at which all powder particles are sintered. Mostly, the bottom layer is left un-sintered and powdery, or the top layer has already melted and shrunk. It is observed that the time interval between polymer sintering point and its melting point is relatively small. These all highlight the importance of heating at the right temperature setting.

Table 3. Factors and levels

Factors	Levels	
	-1	1
T1:Initial Heat temperature (°C)	25-30	45-60
T2: Final heat temperature (°C)	125	130
t: Hold time (min)	2 min	5 min
R: Heating rate (°C min ⁻¹)	5 °C min ⁻¹	10°C min ⁻¹

Design of experiment is used to study involved factors in the process. Due to limited amount of material and time consuming measurements, a fractional factorial design is applied. Table 3, shows involved factors in this process including; Starting temperature (T₁), Final temperature (T₂), Heating rate(R), and Hold time (t). Each run consists of 3 repetitions to reduce the measurement errors. Table 4 shows the design matrix of this process.

Table 4. Design matrix for bulk sintering process (all values in inch metric)

Run	Factors				Avg. shrinkage % after sintering			Y _i	ln Si ²
	T ₁	T ₂	t	R					
1	-	-	-	-	0.004983	0.095728	0.0049825	0.035231	-2.56148
2	+	-	-	+	0.005095	0.004938	0.005095	0.005043	-8.08256
3	-	+	-	+	0.012895	0.01664	0.012895	0.014143	-5.33022
4	+	+	-	-	0.03793	0.074283	0.03793	0.050048	-3.35605
5	-	-	+	+	0.03401	0.034623	0.03401	0.034214	-6.90291
6	+	-	+	-	0.007435	0.0184	0.007435	0.01109	-4.3971
7	-	+	+	-	0.0548	0.051893	0.0548	0.053831	-5.55008
8	+	+	+	+	0.060493	0.022778	0.0604925	0.047921	-3.32409

Measurements are performed by Micro-Vu measuring device. The in-plane dimensional deviation is obtained by measuring shrinkage of the part along x and y axes. This can be further studied to include shrinkage along the z direction. Measuring response is based on the average shrinkage along x and y axes. The orientation of the block has been kept the same during all the experiments to prevent positional errors. Marker guidelines are used on the blocks to help determine the block's positioning and center.

Equations are obtained are as following:

$$\text{Location model: } \hat{y} = 0.01572 + 0.005023 x_{T2} + 0.0052065 x_t x_R$$

$$\text{Dispersion model: } \hat{z} = \ln \hat{\sigma}^2 = -2.46903 - 0.48594 x_R + 0.51742 x_{T1} x_t$$

In order to minimize the dispersion model, the R should be kept at the lower level. Also, based on the T₁ and interaction plots, T1 and t should be set to (+,-). We also need to find the adjustment factor in order to reach our target value which is zero shrinkage. T₂ can be used as an adjustment factor and its value will be calculated as 122.87. Based on material's thermal properties, recommended setting can be provided. Another set of

experiments can be performed to determine the final temperature level. Through our experiments, the final temperature is set at the low level which is 125 °C (Table 5). This setting can be used for future experiments for bulk sintering of the samples to derive the minimum shrinkage.

Table 5. Optimal level setting

Factors	Recommended levels
T ₁	50 °C
T ₂	125 °C
t	2 min
R	5 °C min ⁻¹

Results

It is observed through the first set of experiments that the sintering rate of PA sample was delayed by NaOCl-surfactant and NaOCl respectively. The crystallinity of the pure NaOCl sample has decreased to less than one third of the original PA (Table 6). This is also consistent with the results obtained by bulk sintering of samples up to 125 C with the optimal setting derived under similar condition shown in Table 7.

Table 6. Effect of solutions on the degree of crystallinity of polymer

Sample	Original PA	NaOCl, PA	Surfactant, PA	NaOCl, Surfactant, PA
Crystallinity	0.15731039	0.0460906	0.0892494	0.0561767

Table 7. Effect of solutions on sintering rate of sintered layers of polymer

Sample	Original PA	NaOCl, PA	Surfactant, PA	NaOCl, Surfactant, PA
Sintering condition	Sintered (solid)	Non-sintered/ partially sintered (fragile)	Sintered (solid)	Non-sintered/ partially sintered (fragile)

The combined change in the sintering time and crystallinity of the polymer suggest a change in the polymer chemistry of the polyamide powder. Moreover, the optimal heating setting for sintering samples is obtained.

Conclusion and discussion

The data shown in Table 6 demonstrates the degree of crystallinity of PA samples before and after exposure to the solutions. It reveals that changes in Polymer crystallinity are distinct. A notable increase in sintering period of samples with lower degree of crystallinity was observed during the experiments. Chlorine exposure results in gradual convert of PA's crystalline regions to amorphous state. This partial transform of PA

structure, specifically, polymer chains, lead to longer sintering period. As mentioned before, an ideal inhibitor in SIS process would delay the sintering process up to the temperature at which the desired part body is sintered. Therefore, applying this heuristic method, we can examine an inhibitor's efficiency by monitoring the change in the crystalline state of the treated polymer. This method can be applied to wide class of thermoplastic material to be used in the SIS process. Moreover, through the sintering process, initial temperature, heating rate, hold time, and the final temperature should be taken into account to find the optimal setting. It was shown that starting the sintering process using higher initial temperature, lower heating rate, and lower level setting hold time results in minimum shrinkage of the material.

Future research direction

Although this method is capable of examining a wide range of solutions, there are some limitations which demand further research. After, choosing an inhibitor, printability of the solution in SIS machine should be taken into account. The amount of polymer exposed to the solution might require several depositions on the powder on each layer. Moreover, in-detail exploration of the molecular structure of the polymer chains before and after applying the solutions, gives us better understanding of inhibition phenomenon. FTIR spectra of the sample exposed to NaOCl shows a change in the N-H bonding stretching mode of the PA which can be further studied. Analysis of FTIR spectra helps interpret chemical changes under variety of condition. Moreover, this framework can be further studied to be applied to thermoset material.

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