New polymerization-mixture formulation for jetting: An approach to production of polyamide 6 parts

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Abstract

Poor mechanical properties of manufactured parts is one of the main problems in most of the RP and RM processes. This work deals with a study on formulation of new polymerization mixtures with the aim of being used in jetting process. Two different catalyst components were compared in order to shorten the solidification time and improve the final properties of the manufactured part. The feasibility of jetting polymerization mixtures at jetting head temperature was also investigated. Different characterization and visualization methods (i.e. such as DSC, viscometry, TGA, and hot stage optical microscopy) were used to monitor the polymerization progress and manufactured part properties.

1. Introduction

Rapid manufacturing is defined as 'the use of a computer aided design (CAD)-based automated additive (layer) manufacturing process to construct parts that are used directly as finished product or components'[1]. Among all of the rapid manufacturing (RM) and rapid prototyping (RP) techniques (such as, SLA [2], SLS [3], and FDM [4]), inkjetting has the following advantages: (i) environmentally friendly process, (ii) reduction in material loss and (iii) mass customization [5]. Two different technologies that use inkjet processes have been commercialized; these are the PolyJet[TM] process from Objet and the InVision process from 3D systems [6]. Both techniques use photocurable resins to produce 3D parts (i.e. curing happens by UV radiation of the resin). In the most of the processes, the main obstacle for widespread use of RM is the material properties of the part made. Therefore, having a RM process capable of manufacturing 3D parts with desirable product properties is very advantageous.

In 2007, Additive Manufacturing Research Group (AMRG) in cooperation with Materials Department of Loughborough University initiated a project aiming at

developing a new way of manufacturing 3D polyamide 6 (PA6 or nylon 6) parts. PA6 is one of the main engineering materials in use with a wide range of applications [7]. The main aim of this project is to produce three dimensional objects or components by jetting caprolactam then polymerizing to produce PA6 using the technique of multi-layer printing from a standard jetting head. The intention is to deposit droplets of polymerization mixture A (catalyst + caprolactam) and mixture B (activator + caprolactam) above the melting point of caprolactam from two different jetting heads on top of each other and polymerize on a hot surface. The mechanism of polymerization is anionic ring opening polymerization which is well defined in literature [8-19]. According to different reports, three main parameters play the most significant role in anionic polymerization of caprolactam. These are catalyst (i.e. type and concentration), activator (i.e. type and concentration), and also initial polymerization temperature. Catalyst concentration (two different catalysts used), activator concentration, and initial polymerization temperature were optimized to get the highest monomer conversion, crystallinity, molecular weight, and shortest half-time of polymerization. Since the polymerization mixtures will be deposited in form of very small size droplets (i.e. picoliter volume), the feasibility of drop on drop polymerization is also studied using a small amount of materials.

2. Experimental

2.1 Materials

ε-Caprolactam 99% (MW = 113.16) was obtained from Sigma-Aldrich. The two common catalysts for anionic polymerization of caprolactam, sodium caprolactam (catalyst I) and caprolactam magnesium bromide (catalyst II) were synthesized in our laboratory and employed for polymerization. N-acetyl caprolactam was used as activator and was supplied by Sigma-Aldrich. Cast PA6 samples were kindly supplied by Nylacast, Leicester, UK. All materials were used as received with out further purification.

2.2 Optimizing the polymerization conditions

The optimization was performed with the aid of a randomized standard partial cubic design using ECHIP 7 software with three design variables including: catalyst concentration, activator concentration, and initial polymerization temperature. The response variables are polymerization half time[1], $t_{1/2}$, the final degree of monomer conversion, degree of crystallinity, melting point, and molecular weight of synthesized PA6 samples. These parameters are believed to have the most significant role in controlling the final properties of polymers.

2.3 Equipment and measurements

The viscosity-average molecular weight ($\bar{M}_v$) of PA6 samples was determined by intrinsic viscosity measurement (at a concentration range of 0.001 to 0.005g/ml of PA6/*m*-cresol) with a suspended level viscometer thermostatted at $25 \pm 0.1^{\circ}$C. Differential scanning calorimetry (DSC) was performed by TA Instrument DSC Q200, at a heating rate of 10°Cmin^{-1}, with a temperature range from 20 to 300°C and sample weight of about 20 mg under nitrogen atmosphere. The crystallinity of each sample was calculated by dividing the heat of fusion of each sample by 190Jg^{-1}, which is the heat of fusion of 100% crystalline PA6. The melting temperature, T_m, and polymerization temperature, T_p of each sample was evaluated from the maximum of the endothermic and exothermic peaks respectively. The heat of polymerization was determined by measuring the area under the exothermic peak. Leica-DMLM optical microscope fitted with polarizing filters was used to visualize the polymerization progress. The heating process was carried out using a Mettler-Toledo-FP82HT type hotstage and a FP90 type temperature controller. TGA experiments were carried out using a TA-Instruments SDT 2960 Simultaneous TGA/DSC.

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[1] Polymerization half-time, $t_{1/2}$, here is the time taken for a polymerization solidification process to be half completed. The method to obtain the polymerization half-time is shown in reference [20].

3. Results and discussions

3.1 Optimizing polymerization conditions

Due to the large number of effective variables and parameters in polymerization, ECHIP was used to design experiments. Combination of catalyst / activator has a direct influence on the rate of reaction. This influence can be explained by the fact that the rate of dissociation and therefore the activity of the catalyst decreases with increasing size of the cation due to a decreasing ionisation potential and restricted mobility. A comparison between the efficiency of catalyst I and catalyst II in the anionic polymerization of caprolactam was carried out and results are presented in Table 1.

Table 1: Optimized values for all the parameters

Response parameters	Optimized values	
	Catalyst I	Catalyst II
$t_{1/2}$ (s)	30±5	11±5
T_m (^{o}C)	218±5	223±5
Mon. Con. (%)	95±1	98±1
$\bar{M}_v$ (g/mol)	45,000±10,000	51,000±10,000

It is seen that using catalyst II generated a more efficient catalytic system compared with catalyst I (see Table 2). Using catalyst II resulted in synthesis of polymers with higher molecular weight, final monomer conversion, melting point, and also faster polymerization rate. It was also found in this work that catalyst II is less sensitive to moisture and oxygen as the anionic polymerization of caprolactam can be carried out under normal atmospheric conditions in the presence of catalyst II but not catalyst I.

Results in Table 2 confirm that the anions generated through catalyst formation took part in the polymerization reaction and were not deactivated by moisture or oxygen.

Table 2: Three PA6 sample synthesized in random polymerization conditions: comparison between air and N_2 as the polymerization atmosphere.

Samples[a]		$t_{1/2}$ (s)	T_m (^{o}C)	Mon. con. (%)	$\bar{M}_v$ (g/mol)
1	N_2	15	216	95	24,500
	Air	12.5	216	95	26,000
2	N_2	72	220	97	23,500
	Air	79	219	95	24,000
3	N_2	13.5	217	96	28,500
	Air	12.5	218	96	26,500

[a] All samples synthesized in the presence of catalyst II.

Table 3: Comparison of a commercial cast PA6 with synthesized polymers.

Samples	$t_{1/2}$ (s)	T_m (^{o}C)	Cryst. (%)	Mon. Con. (%)	$\bar{M}_v$ (g/mol)
1	42	219	38	96	48,000
2	34	218	38	96	41,000
3	51	220	40	95	50,000
Commercial 1	5-10min	224	44	94	52,000
Commercial 2	5-10min	223	42	94	45,000

3.2 A comparison with a commercial cast PA6

Three selected PA6 which have been synthesized with the optimized conditions were compared with two commercial cast PA6 samples. Results are presented in Table 3. Results showed a close similarity of properties between a commercial cast PA6 and synthesized PA6 in optimized conditions. It should be kept in mind that the polymerization time is reduced to under 2 minutes in this work. The usual

polymerization time (de-moulding time) in industry is between 5 to 25 minutes depending on the size of the part.

3.3 Polymerization in DSC

The anionic polymerization of caprolactam was investigated using DSC. There are similar investigations in literature [21-25] in which DSC has been used to determine some of the polymerization characteristics such as heat of polymerization and study the effect of different chemical compounds on the polymerization. Thermal behaviour of polymerization mixtures was monitored using DSC. One droplet of each mixture (i.e. A and B about 10mg each) in the molten state were deposited in a cold DSC pan and solidified quickly without undergoing any polymerization reaction between the components. Figure 1 is a thermogram which shows the polymerization process and re-melting of the synthesized polymer after the first DSC run.
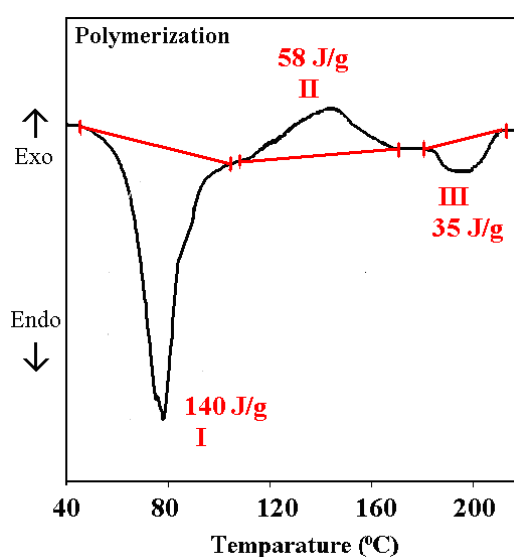

Figure 1: Anionic polymerization of caprolactam in DSC

Three thermal peaks exists in Figure 1 which can be described as follows; peak I corresponds to melting of caprolactam at about $70^{o}C$, peak II shows that an exothermic process which occurred during heating (i.e. onset of this peak is at $110^{o}C$). This peak is associated with the anionic polymerization and crystallization of caprolactam which are exothermic processes. Peak III is at about the melting point of PA6 (i.e. $190^{o}C$ to $220^{o}C$) and confirms that crystallization has occurred during the

heating process. This means that the polymerization and crystallization processes have occurred almost simultaneously.

3.4 Visualization of polymerization progress with optical microscopy

Sample preparation is one of the most important issues that must be considered in hot stage microscopy. The crystalline structure can only be seen when very thin layer of material is being coated between a glass slide and a cover slip, otherwise different crystalline layers interact with each other and result in an unclear image. The anionic polymerization of caprolactam was carried out on a hot stage. The polymerization progress was visualized using an optical microscope fitted with a digital camera. The temperature controller was set heat up the hot stage to $170^{o}C$, at a heating rate of $20^{o}Cmin^{-1}$. The sample remained in the hot stage and was allowed to cool naturally to room temperature. Figure 2 shows the images of the polymerization mixture and synthesized PA6 under a polarized optical microscope.
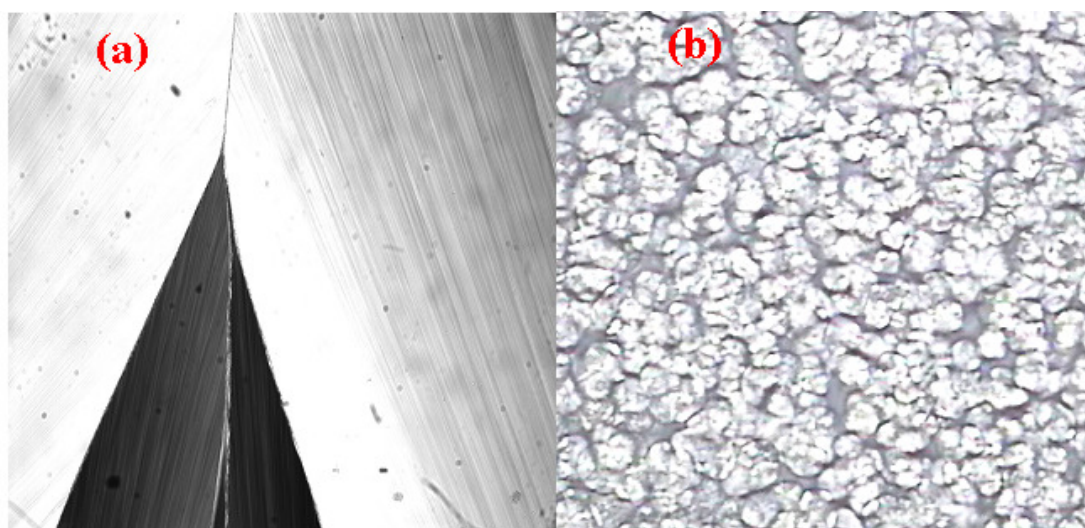

Figure 2: Micrograph of (a) caprolactam crystalline structure, (b) PA6 crystalline structure under a polarized microscope.

The crystalline structure of the polymerization mixture can be seen at $35^{o}C$ in Figure 2a. At $170^{o}C$, the mixtures were totally molten so no light can pass through the polarized filters to the cameras. Spherulite formation was observed during cooling. Since these spherulites were smaller than caprolactam spherulites, it was clear that this was PA6 crystallites. The onset of crystallization was found to be at $130^{o}C$. This is another reason why this crystallization could not be due to crystallization of caprolactam (i.e. caprolactam crystallization point is about $50^{o}C$ and the melting point is about $70^{o}C$). The crystallization of PA 6 showed that polymerization occurred on

the hot stage, however having the crystallization process during the cooling stage showed that the heating rate has been too fast for the PA6 polymerization to be followed by crystallization. Therefore, unlike the DSC experiment, the polymerization and crystallization processes did not occur simultaneously.

3.4 Thermal stability of the monomer

The material lost is important in the case of the surface finish and dimension accuracy of the manufactured part, which seems to be a big challenge in some other RP and RM processes. TGA thermograms were used to study this aspect for caprolactam which is the main part of the polymerization mixture. Determination of caprolactam evaporation rate from small quantities (i.e. about 15-20mg) is important as the monomer will be jetted in the form of very small droplets. The weight change of caprolactam with increasing temperature was measured at two isothermal temperatures (i.e. 160$^{\mathrm{o}}$C and 180$^{\mathrm{o}}$C). Figure 6, and 7 show the weight percentage of caprolactam against time and also the temperature during this experiment at 160 and 180$^{\mathrm{o}}$C respectively.

Figure 6 and 7 shows that the weight loss due to evaporation started at about 130$^{\mathrm{o}}$C and the whole material evaporated within 23 and 18 minutes when the temperature was 160 and 180$^{\mathrm{o}}$C respectively. The evaporation rate of caprolactam at different temperature can also be determined using the slope of the weight loss curve, which is about 7%min^{-1} and 11%min^{-1} at 160 and 180$^{\mathrm{o}}$C respectively. Assuming 130$^{\mathrm{o}}$C as the initial polymerization temperature, the amount of evaporated caprolactam at this temperature would not be significant. Since, onset of polymerization results in suppression of the monomer evaporation, only a small percentage of material is lost before the onset of polymerization. However, if the polymerization takes 30-120 seconds to be initiated, depending on the surface temperature, 3-22% of monomer will be evaporated before converting to polymer.
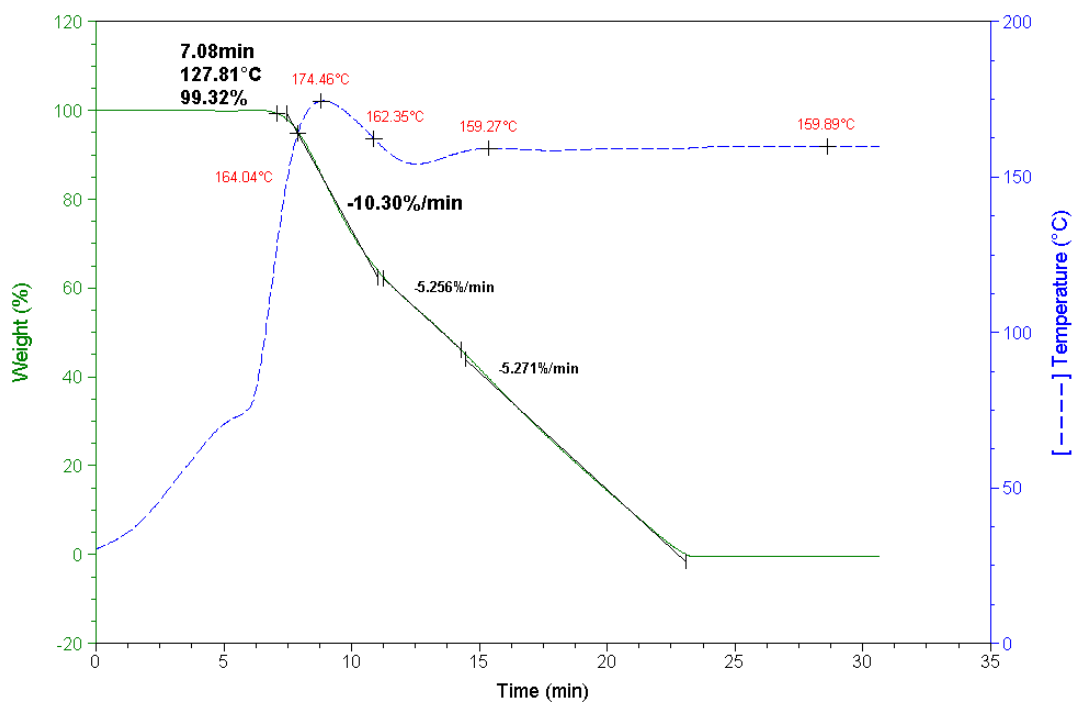
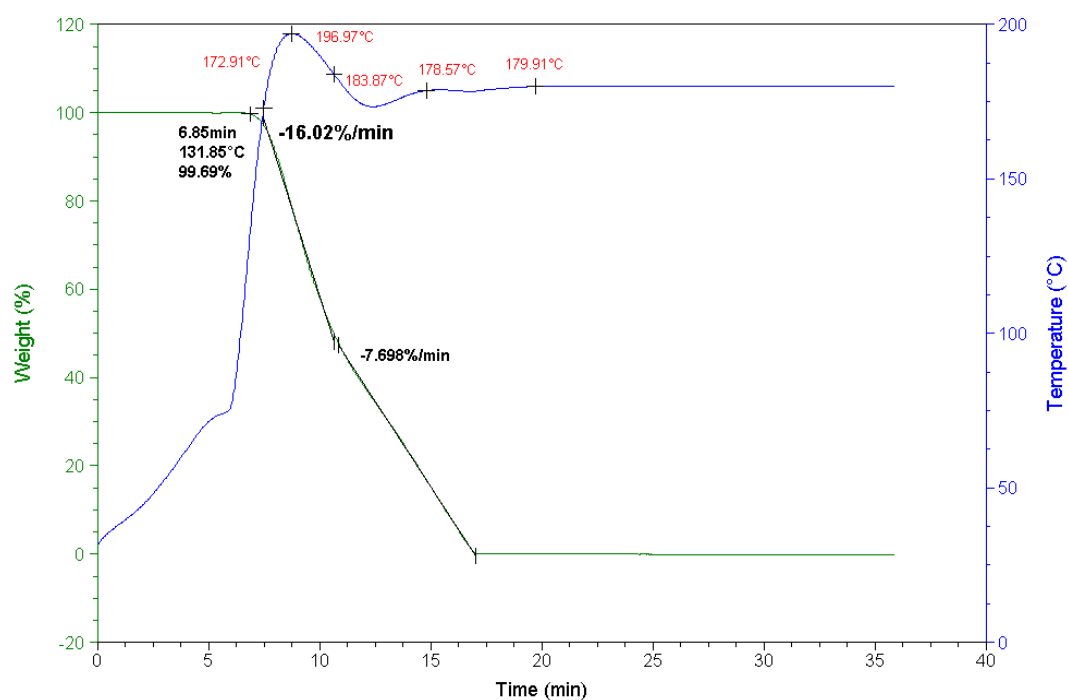**Figure 6:** Thermal behaviour of caprolactam at 160°C.

Figure 7: Thermal behaviour of caprolactam at 180°C

4. Conclusions

Anionic polymerization of caprolactam was investigated in this work. Two different components used to make the catalyst were compared. It was found that catalyst II

was more efficient than catalyst I in this polymerization as it shortened the half-time of polymerization and improved the final properties of synthesized PA6. The properties of synthesized polymers in a fast process were compared with a commercial cast PA6 and a close similarity was found between them. Different characterization and processing methods were used in this work to synthesize PA6 with small quantities of polymerization mixtures. DSC and TGA experiments carried out to study the thermal behaviour of polymerization mixtures. DSC thermograms showed that the polymerization and crystallization processes occurred simultaneously. TGA was used to measure the evaporation rate of caprolactam at different temperatures and predict the amount of evaporated caprolactam after polymerization. Finally, an optical microscope with the aid of a controllable hot stage was used to visualize the polymerization progress. In this case the polymerization process was not followed by crystallization because of the fast heating rate of the hot stage.

5. Acknowledgment

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