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**The structure of parts produced by stereolithography injection mould tools
and the effect on part shrinkage.**

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Abstract

Stereolithography (SL) tooling for plastic injection moulding provides a low cost and quick alternative to hard tooling methods when producing a small quantity of parts. However, work by the authors has shown that a different rate of polymer shrinkage was experienced in semi-crystalline parts when produced from SL moulds as compared to those from conventional metal tooling methods. Different shrinkage means the parts are not truly the same as those that would be produced by metal tooling and highlights a disadvantage to SL tooling.

This work associates the increased shrinkage experienced to a greater percentage crystallinity developed in the parts due to their thermal history during processing. In these experiments the cooling rate, which is imparted due to the

heat transfer characteristics of the mould has been identified as the controlling factor of a parts % crystalline content and the cause of shrinkage anomalies.

The morphology analysis results show that there is ~30% more crystallinity developed in the nylon (PA66) parts produced in SL moulds than those produced from aluminium moulds. The results also reveal different characteristics during thermal analysis that may also be due to the thermal history imparted by the mould.

The work utilises the thermal analysis technique Differential Scanning Calorimetry (DSC) to quantify the different levels of crystallinity in the parts. The thermal characteristics of the mould are demonstrated by real-time data acquisition.

Keywords: Crystallinity, Injection moulding, Polymers, Rapid tooling, Shrinkage, Stereolithography.

Introduction

Stereolithography (SL) is a Rapid Prototyping (RP) process. RP processes directly produce a physical geometry from data derived from a 3D representation (i.e. 3D CAD). They are characterised by generating the geometry by an additive, layer-by-layer manufacturing sequence, which when initiated runs unattended. SL is the most mature commercial RP process, its development began in the mid

1980's. SL represents one of the most geometrically accurate commercial RP processes with a minimum feature size of approximately 0.1mm possible. SL generates a solid object by selectively curing a photosensitive liquid resin by exposure to UV light provided by laser. The part is generated section-by-section on a platform which is contained within the bath of the liquid resin. The materials that can be used in the process are restricted to acrylic and epoxy resins. Resins of very different characteristics are available but they are all essentially variants of epoxy and acrylic (in this work epoxy is used).

Moulds produced by SL have been successfully utilised for the injection moulding of low volumes of parts in various polymer varieties [1, 2, 3, & 4]. The supposed great advantage of the use of SL moulds is that it provides a low volume of parts that are identical to parts that would be produced by conventional hard tooling in a fraction of the time and cost. The technique allows rapid evaluation of a product prior to full-scale production, thus speeding up the product introduction process. However, this work illustrates that different characteristics are exhibited by some parts (crystalline in structure) produced from SL moulds as compared to those from a traditional metal mould. So these revelations defy the greatest advantages of the SL injection moulding tooling process; the moulded parts do not replicate those that would be produced by conventional metal tooling.

This work described in this paper is split into three sections. It begins with a comparison of part shrinkage experienced by two different polymers (crystalline & amorphous) when produced from different mould types (stereolithography & aluminium) (section 1). These results show a significant difference in the shrinkage experienced in the crystalline parts according to the mould type used.

The main focus of this work was to establish the cause of the shrinkage differences in the parts (section 2) and to identify the process variable (section 3) that controls this. The structure of the parts was examined and quantified by heat characterisation analysis with respect to the factor that dictates the shrinkage experienced. The determining process variable experienced by each mould type was illustrated by a data acquisition set-up.

Section 1 – Part shrinkage Evaluation

This section of work has been described in depth in an earlier paper published in the International Journal of Machine Tools & Manufacture [5]. For the purpose of clarity and continuity a brief description of this work is contained in this paper.

The aim of the experiments was to establish the shrinkage that occurs within 48 hours of the moulding of two polymers of very different characteristics (Polyamide 66 and Acrylonitrile-Butadiene-Styrene) when produced by injection

moulding in cavities of differing materials (Stereolithography and Aluminium). This would be by a direct comparison of the dimensions of the moulding cavity and the moulded parts.

1.1 Mould Design

Aluminium was chosen as a metal tooling material for comparison as it represents a common choice when a low volume of parts is required due to the high machining rates possible. The SL moulds were manufactured by a 3D Systems SLA350 machine, using Vantico 5190 resin. The build layer thickness was 0.05mm, as this has previously been demonstrated as an optimal value in extending the working life of SL moulds [6].

The specimen geometry consisted of a bar shape. The bar geometry had dimensions of 12.7mm by 127mm and a wall thickness of 3.2mm. The mould incorporated an open gate design. The draft angle used to ease part removal from the mould was 1.5°. This value has previously been shown to be an optimum value for reducing potential damage to SL tools upon part ejection [6]. No ejection system was utilised in the mould as the parts were simple and easily removed by hand. The mould cavity inserts were contained within a steel bolster which provided alignment of the mould halves, provided material entry into the mould via a tapered sprue bush and protected the inserts from any excessive application of pressure.

1.2 Injection Moulding

The polymers evaluated possessed very different final product characteristics: Polyamide 66 (PA66, crystalline in morphological structure) and Acrylonitrile-Butadiene-Styrene (ABS, amorphous in morphological structure). The PA66 used was Bergamid A70NAT produced by PolyOne. The ABS used was Lustran Ultra 2373 produced by Bayer. Both polymers were hygroscopic and were dried immediately prior to processing.

The injection moulding machine used was a Battenfeld 600/125 CDC model with a Unilog 4000 control unit. This machine consisted of a 60 tonne hydraulic clamping unit and a 125x35mm reciprocating screw injection unit with a conventional tapered nozzle.

In order to isolate experimental variables, it was important to find universal parameter values that would work with both the polymers and both mould material types. The process parameters were identical in all the experiments conducted. Twenty parts were moulded consecutively from each polymer/mould combination.

1.3 Shrinkage Results & Discussion

Shrinkage was evaluated by a direct comparison of the dimensions of the moulding cavity and the moulded parts. The moulds and parts were conditioned

for 48 hours and measured in a laboratory atmosphere of $23 \pm 5^{\circ}\text{C}$ and 50 ± 5 % relative humidity.

The measurements taken from the parts were compared to the measurements of the cavities and expressed as a percentage difference after compensation for thermal expansion of the moulding cavity. The results are shown in Table 1.

The results show that the shrinkage that occurred in PA66 parts from the SL moulds was double that incurred by the comparative parts from the AL moulds while the shrinkage ABS parts were largely unaffected, irrespective of the mould variety. An expected shrinkage range for PA66 is 1 – 2.2% [8]. The parts from the AL moulds demonstrated shrinkage just above the minimum amount expected, while the parts from the SL moulds incurred shrinkage above the maximum in the expected shrinkage range.

Section 2 – Morphology Investigation

This section of work concerned identifying and quantifying the cause of the part shrinkage differences experienced by PA66 parts produced in SL and AL tools.

The most influential factor that determines the amount of shrinkage in

crystalline parts is the amount of crystallinity developed (percentage crystallinity, % χ) during synthesis, in this case heating & cooling during injection moulding [9, 10, 11, & 12]. The crystalline nature (or conversely the amorphous nature) of a bulk polymer has a major effect on its volume/shrinkage. This greater crystallinity is the essential reason why crystalline materials exhibit greater shrinkage than amorphous polymers, due to their nature of having heavily orientated molecular structures. The development of greater crystallinity results in greater shrinkage due to denser packing of the organised molecular chains [13].

2.1 Methodology

The percentage crystallinity (% χ) present in the parts was measured using Differential Scanning Calorimetry (DSC). DSC is a thermal analysis technique used to directly measure the temperatures and heat flow to a sample during heating in a controlled atmosphere over a period of time. This technique provides quantitative and qualitative information about physical changes by monitoring endothermic or exothermic processes that represent material transitions. Specific information that can be obtained includes glass transition temperature and melting point, but most importantly with respect to this work, the measurement of the % χ .

A sample was taken from a central region of four different mouldings from each specimen variety to be examined by DSC and one scan was run on each. The mouldings examined were numbers 4, 8, 12 & 16, from the set of 20

mouldings produced. The sample taken from each of the mouldings was of an average weight of ~17 mg. The mouldings selected for analysis represented an even distribution of the mouldings which were produced in sequence from each experimental variety.

The reasoning for the samples being taken from a central region on the test pieces and not from around the edges or gating areas was to avoid areas whose macromolecular orientation and distribution were influenced by the stress induced by a combination of the melt flow movement and contact with the mould wall. These frozen-in shear stresses result in the part having a very thin surface layer that exhibits different morphological characteristics to the rest of the parts mass [8, 14, 15, & 16]. These skin-like characteristics are common to all injection moulded parts.

One scan was run on each sample. The scan could not be repeated on each sample as the thermal history was erased after each run due to the heating involved in DSC analysis. The samples were extracted from the mouldings by cutting with hand clippers/cutters. By using this method samples were not subjected to heat from mechanical cutting or sawing. Prior to examination, the samples were stored in dessicant crystals. Drying by heating was not used to avoid any possible disruption to the thermal history of the samples.

The apparatus used was a modulated DSC machine produced by TA Instruments, model 2920. The cell atmosphere was provided by a refrigerated nitrogen cooling system produced by TA Instruments. The temperature range of the DSC analysis used was 100-320°C. This operating range was derived by observing the temperatures at which transitions occurred during an analysis in a wider temperature range. This temperature range displayed all transitions of interest while consuming a shorter period of time for each analysis when using a heating rate of 10°C/min.

A value of % χ was derived by quantifying the heat associated with melting (fusion) of the polymer. This area within an example DSC scan is illustrated, along with other characteristics, in Figure 1. The heat of fusion during the crystalline melt can be calculated by determining the area of the endothermic peak [17]. The % χ of the sample can be determined by knowing the heat of fusion for the specific sample and ratioing this against the heat of fusion required to melt a completely (100%) crystallised sample of the material [18]. Such a value for PA66 is 200 J/g [19].

With both these values it is possible to determine the % χ by the equation:

$$\% \chi = \frac{\Delta H}{\Delta H_{100\%}}$$

where: $\% \chi$ = degree of crystallinity

ΔH = heat of fusion

$\Delta H_{100\%}$ = heat of fusion for 100% crystallisation

[20]

2.2 Crystallinity Results & Discussion

The $\% \chi$ results of the samples are shown in Table 2.

An average DSC curve of the samples from each mould variety can be seen in Figure 2 and Figure 3.

The DSC results have shown that there was more crystallinity developed in the PA66 parts produced in the SL moulds than those produced from the AL moulds. The DSC results also showed a slight difference in the curve characteristics displayed by the SL (Figure 2) and AL (Figure 3) mouldings. The AL samples demonstrate an exotherm (crystallization activity, as illustrated in Figure 1) prior to the heat of fusion, whilst none of the SL samples showed this in the DSC tests.

The only variation in the conditions in which the samples were produced are due to the use of a different moulding material, all other process parameters were identical. The heat transfer properties of the mould materials were very different:

SL thermal conductivity: 0.2 W/m-K

AL thermal conductivity: 200 W/m-K

This difference in heat transfer would result in different rates of heat removal from the parts during processing. This rate of cooling is highly influential on the crystallinity which is developed [10, 21, 22, 23, 24] in crystalline polymers. When in their molten stage, all plastics are amorphous (showing little or no organisational uniformity in their molecular structure) and can only regain their crystalline structure after a period of cooling time. Should this period of cooling occur at a very rapid rate the molecules may be unable to re-orientate themselves in such an aligned manner (crystallinity) and remain in an amorphous state. The opposite of this; slower cooling, allows not only re-crystallisation but also the growth of larger crystal structures. Thus the rate of cooling has a great contribution on plastic shrinkage - fast cooling resulting in less crystallisation and less shrinkage, slow cooling in more crystallisation and more shrinkage.

Section 3 - Thermal Conditions Experienced during Moulding

This section of work concerned illustrating the extent of the differences of the thermal conditions experienced in each mould material variety. The differences were quantified by a data acquisition set-up.

3.1 Methodology

The heat transfer rate imposed by each mould type was established by real-time data acquisition during the moulding cycle. Three K-type thermocouples were inserted evenly along the length of the mould. The probe tips were situated 0.5mm below the cavity surface. The signals were read and interpreted by an instruNet data acquisition system, then analysed and recorded with a HP VEE software programme. Prior to polymer injection, each mould was at its ambient temperature of 23.5°C. The temperature profile was plotted over a period of 10 minutes. An average temperature profile was created for each mould variety. These average profiles were generated from the profiles recorded from 20 parts. The consistency between the 20 readings were shown to be within +/- 5% of one another.

3.2 Results

The average temperature profiles experienced in the moulds is shown in Figure 4.

Each of the temperature profiles showed a consistent start temperature of ~23.5°C. The temperature of the environment in which the injection moulding machine was situated was ~18°C. The greater ambient temperature of the mould was caused by a combination of the closed cabinet (completely enclosed safety guarding) and heat from the machine's hydraulic clamping unit where the oil was maintained at a constant temperature.

The SL moulds demonstrate a sudden drop after their temperature peak, at ~48-52 seconds. This was the time of mould opening when the heat in the mould suddenly finds another route to dissipate itself into the air. No such characteristic was displayed in the AL moulds as the temperature peaks after only 2.8 seconds and nearly all activity had ceased by 48-52 seconds.

The profiles illustrate the vastly different temperature conditions experienced in the SL and AL moulds. The temperature activity in the AL moulds occurred in a very short period of time due to the materials high thermal conductivity. The temperature profile in the SL was more extreme and protracted. Without external assistance (i.e. cooling by compressed air) the SL mould would take 15 minutes to return to its ambient temperature.

Conclusions

The shrinkage differences experienced by crystalline polymers has been attributed to a change in morphology (crystallinity), which was caused by a very different cooling rate of the parts. The cooling rate was governed by the heat transfer properties of the mould material.

The results showed that, in comparison with the AL mouldings, approximately 30% more crystallinity was developed in the SL mouldings giving a

total crystalline content difference of approximately 6%. A total percentage crystallinity difference of 2% has previously been shown to have an effect on the shrinkage of other polymers (polypropylene) [25].

The DSC plots (Figure 2 & Figure 3) showed a slight difference in the curve characteristics displayed by the AL and SL mouldings. The AL samples demonstrated an exotherm immediately prior to the heat of fusion whilst none of the SL samples showed this in the DSC tests. The presence of this exotherm was a further indication of the differing percentage crystallinity in the parts produced from moulds of contrasting material type. An exotherm prior to the heat of fusion is due to recrystallisation; the development of further crystallinity in the specimen caused by the heating of the material in the DSC tests. The fact that the samples from the SL mould showed no such exotherm indicate that the sample's thermal history prior to DSC analysis causes the development of maximum permissible percentage crystallinity for the material, unlike the samples from the AL moulds which indicate a lower percentage crystallinity.

It is important to recognise that the $\% \chi$ developed in crystalline polymers dictates many property characteristics of the moulded part, not just shrinkage. Such $\% \chi$ dependant properties include:

- Thermal conductivity (increases with increasing $\% \chi$)
- Strength & stiffness (increases with increasing $\% \chi$)
- Impact strength (decreases with increasing $\% \chi$)

- Density (increases with increasing % χ)
- Transparency (decreases with increasing % χ) [24]

The latter part of this work concerned relating the crystallinity differences, that had been previously demonstrated, to a responsible determinant. It was determined that the cooling rate of the part, which is governed by the heat transfer characteristics of the mould material, was the controlling factor of a parts crystallinity content. The extent of the differences in the thermal conditions experience during moulding have been demonstrated by data acquisition.

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	PA66 Part measurement		ABS Part measurement	
Mould type	AL	SL	AL	SL
% part/mould difference including compensation for thermal	-1.34	- 2.73	-0.76	-0.76

Table 1 – Shrinkage results

Figure 1 – An example DSC curve for PA66

Sample type/name	Heat of fusion (J/g)	Crystallinity (% χ)
AL 1	41.50	20.75
AL 2	43.68	21.84
AL 3	43.48	21.74
AL 4	44.06	22.03
SL 1	56.84	28.42
SL 2	55.71	27.86
SL 3	54.77	27.39
SL 4	56.29	28.15

Table 2 – Heat of fusion & % χ results from DSC

Figure 2 – DSC curve of PA66 from SL mould

Figure 3 – DSC curve of PA66 from AL mould

Figure 4 Average temperature profiles for AL & SL moulds