POLYPROPYLENE MORPHOLOGY IN MICRO-INJECTION MOLDING OF RECTANGULAR GROOVE

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Abstract

In micro-injection molding process, the dimension of the characteristic geometry can be similar to morphological feature size inside the polymer. This work investigates the crystalline morphology in the injection-molded polypropylene parts. It has been found that development of crystalline structure affects the filling flow. The molded micro-structure shows the crystalline growth on the surface. The crystalline structure inside micro-groove can be stretched crystal or spherulite.

Introduction

In injection molding processes, morphological development can greatly affect the quality. It is well-known that semicrystalline thermoplastics shrink more than amorphous ones do because of more packing while crystallization. In micro-injection molding processes, the characteristic dimension can be in the range of 1–100um [1]. Interestingly, the spherulite size of polypropylene (PP) is also in this range. PP is the most versatile thermoplastic with a variety of injection molding grades that are compatible with many different applications. It is expected that PP will allow better mechanical and barrier properties in micro-injection molding parts. Because of aforementioned reason, however, its molding has shown eccentric phenomena, which can limit usage of PP in micro-injection molding.

There are two different kinds of thermoplastics for injection molding. They are amorphous and semicrystalline ones. The molecular chains in amorphous thermoplastics can be oriented along with the filling flow. However, they are randomly arranged and entangled in the solidified parts on the whole. In contrast to amorphous thermoplastics, semi-crystalline ones show partly ordered regions. In this region, the chains are regularly packed by in the molded parts. Microscopically, they are aligned and folded to form a crystalline structure called lamella. In a molded part, the mesoscale feature is characterized by spherulites. This structure is composed of radiating lamellae. In a semi-crystalline thermoplastic, its morphology affects the mechanical and thermal performances. For a molded semicrystalline thermoplastic part to exhibit the desired performance, it should achieve high degree of crystallization.

In injection molded parts, there are three zones through the thickness. In the outer skin zone, the chains are highly oriented along the wall because of two reasons. First, the shear rate is the highest near the wall. Second, the oriented polymer chains are solidified as is without having enough time to relax the shear stress. The polymer solidifies as soon as it touches the wall. On the contrary, in the core zone, the shear rate and cooling rate are low. Thus, the polymer chains are randomly oriented here. When the cooling time is long enough or the mold temperature is sufficiently high, the core zone can be fully spherulitic. Between the skin and the core zones, there is a shear zone with a transcrystalline morphology. The thickness of this zone is proportional to reciprocal of the mold temperature [1-2].

The transcrystalline morphology in the shear zone is non-spherulitic. The well-known shish kebab structure can be formed. Here the shish is the stretched crystalline rod and the kebabs are the epitaxial disks grown from the shish. Under some injection molding conditions cylinders can manifest [2-3].

It has been shown that crystallization can affect micro molding process [5-7]. Flow anomaly can take place when micro-molding flow occur through narrow channel [6]. This work has tried to show the morphological development inside micro-features fabricated by injection molding process.

Experimental

Equipment and Tooling

A two-platen injection mold with temperature control capability has been designed and constructed. The cavity is 40mm by 40 mm with a thickness of 1mm. The cavity is connected to the sprue a side gate and a cold runner system. The mold can accommodate the fabricated mold insert securely.

Then, the mold was attached to a hydraulically operated vertical injection molding machine. Usually, a vertical machine allows for easier experimental setup when mold inserts are placed. The machine in this experiment has injection rate of 57cc/s, injection capacity of 83cc and screw stroke of 135mm. Moreover, it has clamping force of 60 ton and clamping stroke of 230mm.

Fig. 1 Design of mold insert and fabrication plan.
To conduct a micro-injection molding experiment, a mold insert with simple micro-patterns, as shown in Fig. 1, has been fabricated. This mold insert is usually called stamper as in hot stamping process. The micro-pattern here is a rectangular groove with a draft angle formed during lithography process. Anisotropic etching process using KOH solution was employed to realize micro-channel on a Si wafer. This process allows an aspect ratio up to 1:5. To fabricate a mold, Ni electro-plating was performed afterwards. This etching process is comprised of the following steps: (1) Coat the photoresist material on top of the Si wafer with SiNi cladding together with a prepared film mask followed by baking processes; (2) Remove the SiNi cladding selectively by the reactive ion etching process; (3) Etch out the Si wafer under KOH solution. To fabricate a durable mold insert, the wafer was nickel-plated to approximately 0.5mm followed by separation, trimming and grinding. Figure 2(b) shows the finished mold insert.

On the stamper, the fabricated channel widths, which is indicated in Fig 2 (c), are in the range between 15µm to 138µm. The measured draft angle is in between 88.9° and 89.3°. The depths are identical for all grooves 52µm.

Material

In this work, serveral different materials have been tested to find out the molding the remainder of the paper. To compare PP with other semicrystalline and amorphous thermoplastics, two more thermoplastics other than PP are selected. They are HDPE and PMMA. Because HDPE is still semicrystalline but the crystalline features are order of magnitude smaller than the groove size, they are not expected to influence the flow during micro-injection molding. Not to mention, PMMA would not either. This will be verified again later in this paper. Table 2 shows the thermoplastics tested here.

<table>
<thead>
<tr>
<th>Material</th>
<th>Description</th>
<th>MI, g/10min</th>
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<tbody>
<tr>
<td>HDPE</td>
<td>injection molding</td>
<td>5 (190°C, 2.16kg)</td>
</tr>
<tr>
<td>PMMA</td>
<td>injection molding</td>
<td>5.5 (230°C 3.8kg)</td>
</tr>
<tr>
<td>Homo PP</td>
<td>injection molding</td>
<td>10 (230°C, 2.16kg)</td>
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Microscopy

The molded micro-structures are examined with microscopy. First, the molded grooves are examined with conventional optical, polarized optical (POM) and scanning electron microscopies (SEM) [1].

Results

Flow front

Figure 3 shows the microscopic image of molded structure. Figure 3(b) shows an eccentric pattern which is not observed in Fig. 3(a) and(c). A lot of experiments which are not presented here were conducted so far. However, none of the results with HDPE and PMMA has shown any instability. This paper is going to explain why this is taking place only in PP. The SEM image in Fig. 4 shows what exactly happens during PP melt flows in a micro-channel. Something eccentric has been observed here. Balls are created on the front of inside groove flow.
Figure 4. PP flow instability observed for melt temperature of 230°C, mold temperature of 125°C and pressure of 600bar (PP).

The fabricated groove looked as if teeth are grown up on the gum, which means the ball formation takes places after substantial advance of normal flow front. Although the spacing is not strictly uniform, the balls are periodically created over the entire groove length.

(a) Top view of 80µm groove

(b) Top view of 32µm groove

Figure 5. Molded results for different groove dimensions at mold temperature of 120°C.

The flow progress is quite extensional and the flow is impeded by the elastic tension not by the wall shear stress [8-9]. The tension is fairly strong that the flow front has a tendency to be stagnant for a moment while pressure is building up. While the melt front is stagnant, the temperature on the front becomes lower and elastic skin layer is formed. In the meantime, the melt inside, still under high temperature and high pressure, experiences high normal and shear stresses because of the high shear rate [10-12]. At a weaker point of the elastic skin layer, it is penetrated by pressurized inside melt. The flow will not be uniform over the channel entrance.

Figure 6. Crystalline structure near micro-groove of 30µm (PP)

The flow would be very extensional. Fig. 6 shows a stretched crystalline line inside a micro-groove. It can be seen that still crystals are developing in the radial direction centering the stretched line.

Two important observations have already been reported in [5-6]. First, there is a critical channel width where this instability happens. Second, the onset of this unstable front is more distinct for higher temperature. Thus, the balls in Fig. 4 and Fig. 5(b) are attributed to crystallization of PP.

Figure 7 Micro-groove with 25µm molded at 100°C (PP)

Crystalline Structures
As shown in Fig.6 and as can be seen other papers, in the core region, spherulites are observed. The size of spherulites are smaller near the wall. Near the groove entrance cylindrites are found. Those cylindrites are pushed into the micro-groove and they are stretched inside while this extensional contracting flow.
Moreover, from the stretched crystal, new spherulitic structure can grow inside the groove. As shown in Fig. 7, a new spherulite is growing at the end of the groove and that have formed the balls in Fig. 4. Note that in molding with HDPE, it is very difficult to identify the spherulitic structures under the same molding condition and with the same POM method. This should be due to the smallness of their sizes.

It should be also noted that the heating of mold surface makes the skin zone very thin. This is another important feature of micro-injection molding. Instead, thick cylindrites zone is created near the mold wall.

**Implications in injection molding**

In conventional injection molding processes, crystallinity increases shrinkage, narrows process window, reduces optical clarity, and so on. On top of these issues, this work has shown that filling process can be complicated in micro-injection molding because of morphological developments. There can be some reasons for micro-molded parts to be made of semicrystalline thermoplastics. For example, if liquid flows through the channel, it needs better barrier property. If the channel is pressurized, the channel requires enough mechanical strength. If the fluid is hot, it should be more thermally stable. For the same reason semicrystalline polymers are selected for conventional parts, they are selected for micro-parts.

If the characteristic dimension of morphology is similar in scale with geometric dimension, this flow anomaly can happen. For some products, although this happens, the part can satisfy the requirements as long as this anomaly does not dimensionally and visually damage the final part. However, for some, the part can fail to satisfy them. For example, the micro-welds due to the balls can make the channel weaker than the required.

To cope with this, there can be two ways. The first is to change or modify the material to allow for smaller crystalline sizes. The second is to control the process to suppress such crystalline developments. The second approach will be very limited in actual production cycles.

**Conclusions**

The micro-injection molding characteristics of PP have been scrutinized here. To investigate the flow instability during the micro-injection molding, a micro-mold insert has been fabricated and assembled to an injection mold. The mold insert has deep straight rectangular grooves with constant width and depth. The molding experiments have shown that the instability took place only with PP resins and not with HDPE and PMMA.

The unstable flow front inside the groove forms many periodic balls. This work has shown those balls are due to spherulitic crystallization of PP. It has also been found that those spherulites on the flow fronts are stretched cylindrites which are inherently similar to those near the macro-cavity wall.

There is a critical channel width where the instability starts to show up. When the temperature was low, the onset transition of instability ranges over a wide interval. On contrast, when the temperature was high, the transition was more discrete. The crystalline structure inside the groove would be also affected by the groove width. This needs further investigations. In some of the POM images, only spherulitic shapes are observed while helical structures are found in other images. The eccentric flow front propagation is related to the rheological difference between intra-spherulite and inter-spherulites.

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**References**