Fundamental Study on Structure Development of Thin-Wall Injection Molded Products

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Thin-wall injection molding of polypropylene (PP) was performed to clarify the structure and mechanical properties of micro-scale molded products. Effects of mold thickness and process conditions on processability in micro injection molding were evaluated. Furthermore, the structure and mechanical properties of molded products were analyzed using wide angle X-ray diffraction, birefringence, DSC measurements, and tensile testing. The molecular orientation in the vicinity of the gate was higher than that at any other positions. Birefringence increased with decreasing mold temperature, whereas crystallinity decreased with decreasing mold temperature. Results of cross-sectional observation also revealed a skin-core structure inside the molded products; spherulite structure at core region was not observed at thin cavity thickness at low mold temperature. The thickness ratio between the thickness of skin-shear layers and total cavity thickness increased at thinner cavity thickness. Elongation at break of the products with cavity thickness of 0.3 mm became higher with decreasing mold temperature.

1. INTRODUCTION

Polymer processing, especially injection molding process, is an ideal process for mass-production. For that reason, it is widely used in various industrial situations in the automobile, electrical, and food packaging industries. In recent years, quality improvement and higher performance of molded products are keenly required, especially for precise and micro-scale products such as optical devices, medical applications, information and communication applications, and others. These micro-scale system technologies (MST) will have a far-reaching influence on device manufacture in the near future. MST is also described as micro electro mechanical systems (MEMS). During the last two decades, numerous studies have addressed the research and development of MEMS. An intense research interest has prevailed in precision polymer processing for miniature products because of the growing emphasis on MEMS 1-6. One of important technology for production to the functional materials and base parts of MEMS is micro-scale polymer processing. Micro-scale polymer processing, i.e., micromolding, is roughly divided into three categories: the first is production for the molded product with surface structure of the size of a micro scale, the second is production for micro scale weight product, and the 3rd is production for the super-thin wall molded product with the micro-scale thickness. However, micro-scale polymer processing technology is still in a trial and error stage. Moreover, it is difficult to achieve an optimum product design. Most studies have limited their scope to issues of processability and surface structure observation; the structure and properties of the molded products have not been deeply discussed. Molding conditions have a marked effect on structural development and final properties of molded products. Therefore, precise investigation of relationships between molding conditions and structure and physical properties is indispensable.

Thin-wall micro-scale injection molding was carried out in this study. Structural and physical properties of molded products were investigated. By changing the mold wall temperature and the cavity thickness, their effects on the structure and properties were studied systematically using various measurements.

2. EXPERIMENTAL
2.1 Material and injection molding process

Isotactic polypropylene (PP, F-704NP, MI=6.8) used in this study was kindly supplied by Idemitsu Kosan Co. Ltd. Usually, shear viscosity is so low that MI is high, and it is easy to flow. However we used this polymer because this PP was well investigated to a molecular weight, a molecular weight distribution, tacticity, viscosity, a thermal property, etc, the crystalline-nucleus agent is not contained.

We used the intelligent process analysis system for micro-scale injection molding, which consists of a micro-scale injection molding machine and material properties measurement apparatus?). A small electric injection molding machine (ELJECT AU3E; Nissei Plastic Industrial Co., Ltd.) was used for molding. It has maximum clamping force, injection speed, injection pressure, injection volume of 29.4 kN, 300 mm/s, 250 MPa and 1.4 cm3, respectively. The injection system of the machine is composed of a screw barrel for plastication and a plunger injection system. The screw diameter of the plastication unit is 14 mm. A 8 mm diameter injection plunger is employed for melt injection.

The temperature of the injection unit was 220°C, and the injection speed was 110 mm/s. The injection and cooling times were 3 and 10 s, respectively. The maximum injection pressure was 55 MPa. The mold temperatures chosen in this study were 40, 70, and 100°C.

The shape of molded product prepared in this experiment is shown in Fig. 1. The mold is rectangular with full length of 60 mm and width of 5.5 mm. The mold has different cavity thickness between the gate region and central region. The cavity thickness around the gate is 1.0 mm. The length of this region is 10 mm. On the other hand, the cavity thickness of the central region was varied to 0.1, 0.3, 0.5, and 1.0 mm. The length of this region is 40 mm. Here, we defined that the vicinity of the gate is position A. The product end that is distant from the gate is position C. The central part between A and C is position B.

2.2 Structure and properties of molded products

We investigated processability through flow length measurement of molded products using a digital camera, polarizing filter and a magnifying glass. Measurements of birefringence, wide angle X-ray diffraction, and differential scanning calorimeter (DSC) were also performed; thereby, we analyzed the molecular orientation and crystal structure. The dumbbell specimen was cut down from the central part, 40 mm length portion of a molded product. Thereafter, tensile testing was performed.

![Fig. 1 Shape of molded product.](image)

3. RESULTS AND DISCUSSION

3.1 Shape and polarized photograph of molded products

We observed the products using the polariscope. Figure 2 shows photographs of molded products. In the case of 0.3 mm mold cavity thickness, the flow length of the product was around 40 mm for all process conditions. On the other hand, in the case of 0.1 mm cavity thickness, the flow length was about 5 mm. The flow length decreased with decreasing the cavity thickness. When cavity thickness becomes thinner, a cooling rate for melted resin increases. At higher cooling rate, the viscosity of melted resin abruptly increases and
solidification of melted resin occurs rapidly. The flow length becomes short because of an increase in viscosity and rapid solidification for melted resin.

Furthermore, we observed the interference fringe patterns under a crossed-polarization condition. An interference fringe correlates closely with optical retardation, optical retardation increased with decreasing mold cavity thickness.

3.2 Crystalline structure and crystallinity

The WAXD patterns of an injection molded products are shown in Fig. 3. The X-ray diffraction was observed by irradiating X-ray beam perpendicular to a MD-TD plane, and the overall diffraction was contributed from internal structure distribution. The mold temperature was 40°C. We observed c-axis and a*-axis crystalline orientation at each point. Molecular orientation in MD direction is particularly high at position A in the vicinity of the gate because of the high shear rate in this region. They showed a similar tendency to that of the case of a common injection molded PP. However the crystalline diffraction tended to concentrate on the equator with a decrease in cavity thickness indicating that there is a considerable development of molecular orientation, and the molecular orientation is so high such as high-speed spun fiber at 0.1 mm cavity thickness. Crystallinity calculated from the result of DSC measurement is shown in Fig. 4. Crystallinity was about 40%; and in the vicinity of the gate showed a slightly higher value. This behavior was similar to the molecular orientation. Furthermore, a lower mold temperature led to a lower crystallinity. At lower mold temperature, high shear stress led to high molecular orientation. However, since PP has high crystallization rate, crystallization behavior is not simple under non-isothermal and high shear flow such as injection molding condition. Crystallinity usually shows about 30 to 50% even if molding conditions change. On the other hand, when the cavity thickness increased as 0.5 and 1.0 mm, crystallinity showed almost identical values at all positions. Although following section describes in detail, structure distribution was shown inside of the molded products. We think that crystallinity was a little high at skin and shear layers. It was considered that the difference in crystallinity was based on the influence of that structure distribution.

3.3 Birefringence and skin-core structure

Figure 5 shows birefringence in the MD-TD plane of a molded product. Birefringence of the molded product was low at position C which is the flow end, and birefringence became higher at positions A and B. Moreover, birefringence showed the highest value at the lowest mold temperature. In general, the optical anisotropy increases with decreasing mold temperature because of the increasing in shear stress of the melt resin in the flowing process. However, these values of birefringence were an average of the thickness direction.
Fig. 3  WAXD patterns of molded products at positions A and C. Mold temperature is 40°C.

Fig. 4  Crystallinity profiles of molded products. Cavity thickness is 0.3 mm.

Fig. 5  Birefringence profiles of molded products. Cavity thickness is 0.3 mm.

ND. The injection-molded product commonly has structure distribution inside the molded product.  
Molecular orientation in the skin layer near the surface becomes higher than that of the core layer which is inner part of molded products.

In order to analyze the skin-core structure of molded products, thin section cut parallel to the MD from the molded products. Cross-sectional views of the molded products observed under polarizing microscope are
shown in Fig. 6. Thin section cut parallel to the MD from the molded products. The mold temperature and thickness are 40°C and 0.3 mm, respectively. A clear skin-core structure composed of a surface skin layer with a high molecular orientation and an inner core layer with low molecular orientation is observed. The thickness of skin layer was around 0.07 mm at position A. At the position C located in the distance from a gate, the middle layer between the skin and core layer called a shear layer was observed. It showed a similar tendency to that of the case of common injection molded PP product with thick cavity thickness. However spherulite structure at core region was not observed at thin cavity thickness at low mold temperature. From these observation of cross-section of molded products, the thickness of skin and shear layers at position A slightly increased with increasing cavity thickness, but the thickness ratio between the thickness of skin-shear layers and total cavity thickness increased at thinner cavity thickness. Accordingly, this means that the core region was reduced with decreasing the mold cavity thickness, and the molecular orientation in the core region becomes higher.

3.3 Mechanical properties

Figure 7 shows the stress-strain curve of the molded products. Elongation at break of product prepared with the mold temperature of 70°C decreased with decreasing cavity thickness. In case of 1.0 mm thickness, elongation at break of product prepared with the mold temperature of 100°C was the lowest as compared with those of 40 and 70°C. At 1.0 mm, the molecular orientation of molded products at 100°C was lower than those of 40 and 70°C. Moreover core region became thicker and spherulite structure occurred in the region. In case of 0.5 mm thickness, elongation at break of product prepared at 100°C was the highest as compared with those of 40 and 70°C. This shows an opposite behavior to that of molded product of cavity thickness 1.0 mm. At high mold temperature of 100°C, Young’s modulus and tensile strength of products became lower as compared with these of lower molding temperatures. In case of 0.3 mm thickness, elongation at break of product at low mold temperature of 40°C became higher than those of 70 and 100°C. Furthermore, Young’s modulus of product at low mold temperature of 40°C was slightly lower than those of 70 and 100°C. In the molded product which has slightly molecular orientation, these mechanical properties have closely relation to high order structure, and Young’s modulus and tensile strength increase with increasing molecular orientation and crystallinity. At 0.5 mm thickness, it is reasonable in the relation between molecular orientation and a mechanical behavior. However, in the case of injection molded products of 0.3 mm thickness, it was the involved behavior that ductile brittleness transition had occurred. As described above, the molded products have the structure distribution such as skin-shear-core, and structure also changed with the positions of a molded product. In this study, mechanical properties are evaluated as an average value of the thickness direction and a position of a molded product. We found that the involved mechanical characteristics were affected by the internal structure distribution of a molded product.

4. CONCLUSION

We performed thin wall injection molding, and the structure and physical properties of PP molded products were investigated. The molded products were produced at various mold temperatures and mold cavity
Fig. 7  Stress-strain curves of the molded products. Cavity thicknesses are a) 1.0 mm, b) 0.5 mm, and c) 0.3 mm, respectively.

thicknesses; the effects of molding conditions and mold thickness on high-order structure and physical properties were examined with micro-scale.

When cavity thickness became thinner, the flow length decreased because of an increase in viscosity and rapid solidification for melted resin. From these result of WAXD and birefringence measurement, c-axis and a*-axis crystalline orientation at each point was observed, and it showed a similar tendency to that of the case of common injection molded PP. Molecular orientation in MD direction was particularly high at the vicinity of the gate because of the high shear stress in this region. Molecular orientation increased with a decrease of cavity thickness. However it showed the same high molecular orientation as high-speed spun fibers at cavity thickness 0.1 mm. Results of cross-sectional observation also revealed a skin-core structure inside the molded products. However spherulite structure at core region was not observed at thin cavity thickness at low mold temperature. The thickness ratio between the thickness of skin-shear layers and total cavity thickness increased at thinner cavity thickness. Results of tensile test showed that elongation at break of the molded products of cavity thickness of 0.3 mm was lower compared with those of 0.5 mm and 1.0 mm, and it is closely related to internal structure distribution.

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