Correlation Between Flow Mark and Internal Structure of Thin PC/ABS Blend Injection Moldings

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SYNOPSIS

The purpose of this study is to clarify a mechanism of the flow mark that appears on the surface of thin PC/ABS blend injection moldings through the observation of the internal structure at various processing conditions. The flow mark had two different constitutions, such as a luster part and a cloud part, alternately on the both surfaces. It was obvious that the luster part was a PC-rich state, and both the PC and ABS coexisted at the cloud part from the surface analysis of the article. The internal structure of the flow mark article was quite different from no flow mark article. In the case of no flow mark article, a clear fountain flow could be seen at the flow front, and the ABS could not be seen at the tip of the flow front from the observation, whereas in the case of the flow mark article, the center of the flow front went towards the mold thickness direction. As a result, the PC phase, which covered at the tip of the flow front, might be broken, and both PC and ABS coexisted, and thus formed the flow mark. Moreover, in the case of the flow mark article, it was found that the PC and ABS had already flowed with winding while they entered the mold cavity from the gate. Therefore, a designing for the gate may be most important to control the flow mark. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Thin injection molding is expected to obtain small and light-weight products. 1-3 Particularly for OA machinery or communication apparatus, such as portable computer, pocket telephone, and so on, the requirement of thinning the thickness becomes higher. Moreover, thinning is quite variable for a low cost because of low material using and enhancement of processability due to a short cycle of cooling. On the other hand, thin injection molding may be difficult, and various improvements for processing are required. For example, from the view point of materials, polymer blends have been widely used to improve not only processability but also physical properties of injection moldings. However, thin injection moldings may have several molding defects. For example, a dimensional defect such as a sink mark and warp, or a surface defect such as a flow mark and silver streak often appeared. Among these

In this study, the flow mark on polymer blend thin injection moldings was investigated. The material used was a PC/ABS blend, which is widely used for housing articles. Thin PC/ABS blend injection moldings, which have less than 1 mm, were fabricated, and the mechanism for appearance of a flow mark was clarified through precise observation of the internal structure of the injection moldings.

EXPERIMENTAL

Material and Processing Conditions

The PC/ABS blend (Cycoloy C1000) was supplied by General Electric Plastics, Japan Co., Ltd. The sample was injection molded using a Nestal SG150 (Sumitomo Heavy Industries Ltd.) injection-molding machine, and a dumbbell-shaped sample was fabricated. The processing conditions are listed in

molding defects the studies of a flow mark are very few, and the mechanism of flow mark appearance has not been clarified quantitatively in spite of this most serious problem.⁴⁻⁸

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Table I Processing Conditions

| Cylinder Temp. (°C) | | | | Cavity | Injection | |
|---------------------|-----|-----|-----|---------|-------------------------------|--|
| #1 | #2 | #3 | #4 | Temp. | Speed (cm ³ /s) | |
| 280 | 270 | 260 | 260 | FO 110 | 35, 45, 53 | |
| 300 | 290 | 280 | 280 | 70, 110 | | |

Table I. The processing conditions were: cylinder temperature, 280°C and 300°C; cavity temperature, 70°C and 110°C; and injection speed, 35, 45, and 53 cm³/s. Figure 1 shows schematic representation of the sample. The thickness of the sample was 1 mm.

Surface Analysis

The surface morphology was examined by using scanning electron microscopy (SEM) (JEOL, model JSM-5200). Prior to observation, the ABS component was etched out in a chromic acid mixture, and the sample was coated with gold. The etching agent was made by mixing 30 mL of aqua, 120 mL of sulfuric acid, and 5.0 g of chromic acid. The sample was immersed in 80°C of the agent for 8 min. Details of the etching technique can be found in recent studies. Next, hardness on the surface of PC/ABS, PC, and ABS was measured by using a hardness testing machine (SHIMADZU HMV 2000), and surface structures of the samples were also examined. The constructions of the surface were examined by using a FTIR ATR measurement (Nicolet FTIR 20 DXB).

Observation of Internal Structure

The cross-section morphology along the longitudinal direction of the samples was also examined by SEM after etching by using a chromic acid mixture. The same observation of the flow front region of short-shot injection moldings was also examined, and flow behavior of a PC/ABS blend in mold cavity was investigated.

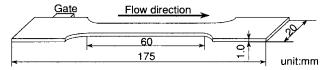


Figure 1 Schematic representation of the sample.

Table II Results of Flow Mark Appearance

| Cylinder Temp. (°C) | | | | Cavity | Injection | |
|------------------------|---------------------------------------|-----|-----|--------|-------------------------------|--------------|
| #1 | #2 | #3 | #4 | Temp. | Speed (cm ³ /s) | Flow Mark |
| | | | | | 35 | X |
| | | | | 70 | 45 | X |
| | | | | | 53 | X |
| 280 | 270 | 260 | 260 | | | |
| | | | | | 35 | X |
| | | | | 110 | 45 | X |
| | | | | | 53 | X |
| | | | | | 35 | 0 |
| | | | | 70 | 45 | X |
| | | | | | 53 | X |
| 300 | 290 | 280 | 280 | | | |
| | | | | | 35 | 0 |
| | | | | 110 | 45 | 0 |
| | · · · · · · · · · · · · · · · · · · · | | | | 53 | X |

RESULTS

Appearance of the Flow Mark

Table II shows the results of flow mark appearance. A circle (O) in the table expresses the case where a flow mark did not appear, and a cross (X) expresses the case where a flow mark appeared. In the case of a low cylinder temperature, a flow mark appeared on the surface of samples regardless of mold cavity temperature and injection speed, whereas in the case of a high cylinder temperature, the appearance of a flow mark was influenced by the mold cavity temperature and injection speed. A flow mark has two different constitutions, such as a luster part and a cloud part, alternately on the both surfaces, as shown in Figure 2. It was obvious from these results that low cylinder temperature, low mold cavity temperature, and high injection speed are factors of flow mark appearance.

Surface Structure

Surface structure of a flow mark after etching as revealed by SEM micrographs is indicated in Figure 3. Figure 3(a) and (b) show the luster part and cloud

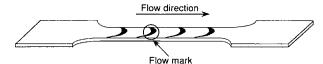


Figure 2 Schematic drawing of a flow mark.

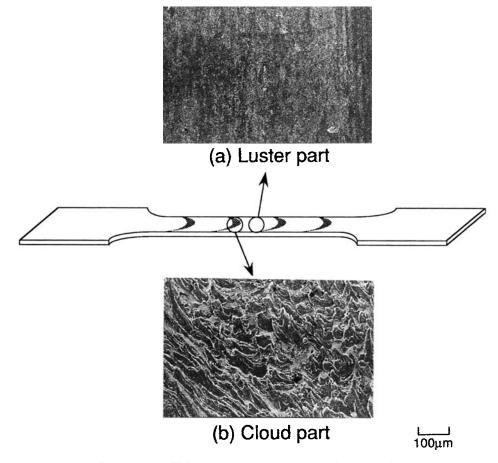


Figure 3 SEM micrographs of a flow mark after etching.

part, respectively. The structure of the luster part is apparently different from that of the cloud part. The luster part has a flat surface, whereas the cloud part has a rough surface due to etched-out ABS components. It appears that the luster part is a PC-or ABS-rich state, because it has two predictions for this phenomenon. One is that the PC remained and the surface did not etch out. Another is that all the ABS was etched out and the surface became flat. On the other hand, it was clear from this observation that the cloud part coexisted with the PC and ABS.

Table III lists results of the hardness test. A hardness test was carried out for the luster part and

the cloud part before etching, the luster part after etching, the PC, and the ABS. Scatter of the hardness at the cloud part was larger than that of the luster part. It appears that the luster part has a uniform surface structure, whereas the cloud part has a nonuniform structure. This result corresponds with previous observation results of the surface. Values of hardness were not different at the luster part between the before-etching sample and the after-etching sample. This means that the structure of the luster part does not change by etching, so that the PC may be a rich state at the luster part.

Figure 4 shows FTIR ATR spectra of the luster

Table III Results of Hardness Test

| | Before 1 | Etching | | | |
|----------|-------------|------------|---------------------------|-------|------|
| | Luster Part | Cloud Part | After Etching Luster Part | PC | ABS |
| Hardness | 13.6 | 13.32 | 13.78 | 17.27 | 3.46 |
| CV (%) | 1.47 | 5.33 | 1.41 | 2.92 | 4.29 |

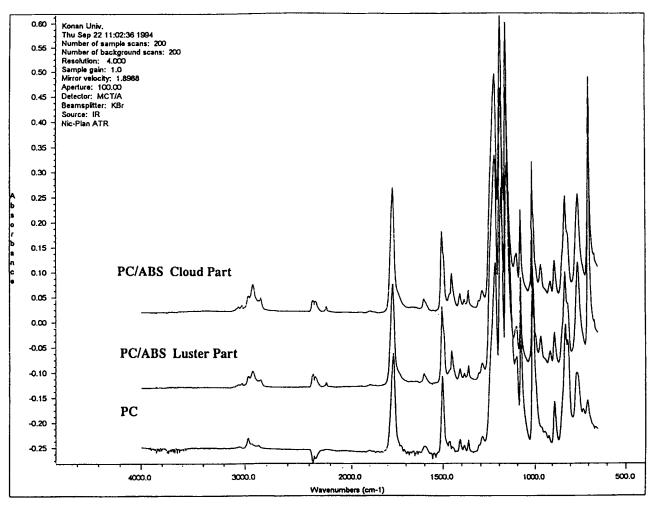


Figure 4 FTIR ATR spectra of the luster part, the cloud part, and the PC.

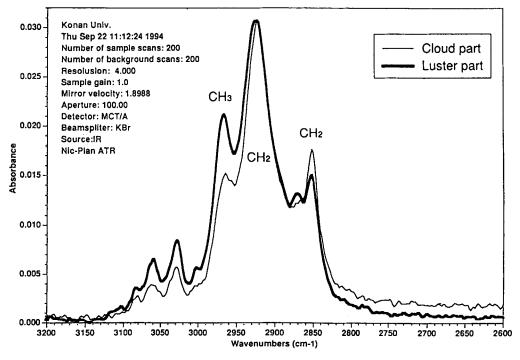


Figure 5 FTIR ATR spectra of the luster part and the cloud part.

part and the cloud part. As a reference, the spectra of PC is indicated simultaneously. The IR spectra of the luster and cloud parts were not very different from that of the PC. However, the IR spectra were different in range of wave numbers between 3200 cm⁻¹ and 2600 cm⁻¹. Therefore, the difference of constitution between the luster part and the cloud part was investigated from absorbancies of CH₃ and CH₂, which were included in this range. Figure 5 shows the IR spectra of the luster part and the cloud part in a range of wave numbers between 3200 cm⁻¹ and 2600 cm⁻¹. The spectrum of the luster part was different from that of the cloud part. The CH3 absorbance of the luster part was higher than that of the cloud part, whereas the CH₂ absorbance of the luster part was lower than that of the cloud part. It is considered the the PC content is higher and the ABS content is lower in the luster part than the cloud part, because CH₃ is one of the components of PC, and CH₂ is one of the ABS components. Therefore, it was obvious that the luster part and the cloud part had different structures.

Internal Structure

Figure 6 shows SEM micrographs of cross-sections along the longitudinal direction (i.e., flow direction) of the flow mark article. The ABS components were etched out and became halls. However, etched-out ABS components cannot be seen at the skin layer of the luster part side. It appears that the luster part is a PC-rich state. On the other hand, etched-out ABS components can be seen at the skin layer at the cloud part side. Therefore, PC and ABS may coexist at the cloud part. The PC phase and ABS components are orientated along the flow direction at the internal region of the sample, and heterogeneous distribution of each phase can be observed through the thickness direction. In the case of no flow mark article, the etched-out ABS components cannot be seen at both surfaces of the article, as shown in Figure 7. It seems that the PC is a rich state at both surfaces. At the internal region of the sample, same tendency of the PC phase distribution can be observed. However, both the PC phase and ABS components are orientated straighter along the flow direction than the flow mark article. From this result, the flow behavior of resin is different between these articles, and this difference may be concerned with the appearance of the flow mark.

Flow front observation along the flow direction of each article is examined. Figure 8 shows SEM micrographs at the flow front region of both articles. In the case of the flow mark article, the PC phase

Flow mark article

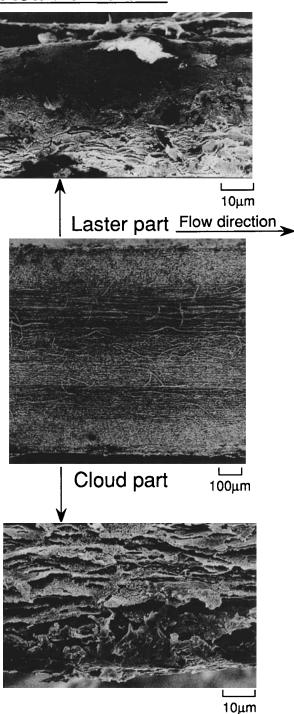


Figure 6 SEM micrographs of a cross section along the logitudinal direction of a flow mark article.

orientated along the flow direction with winding and a clear fountain flow cannot be seen, so that the center of the flow front goes towards the mold thickness direction. At the tip of the flow front both PC

No flow mark article

Flow direction

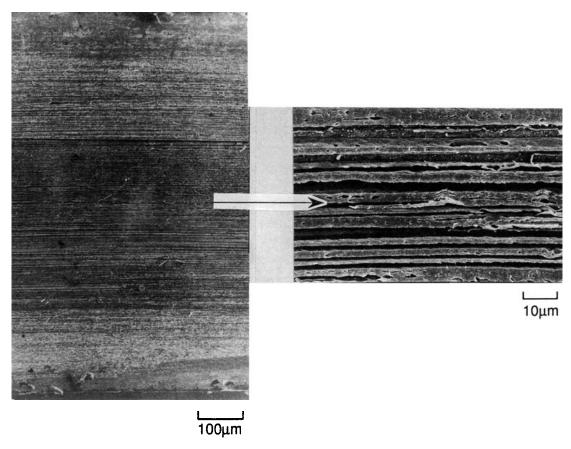


Figure 7 SEM micrographs of a cross section along the logitudinal direction of a flow mark article.

and ABS components coexist. An abnormal fountain flow may occur from these phenomena, whereas in the case of high cylinder temperature, a fountain flow can be seen clearly at the flow front, and the ABS components cannot be seen at the tip of flow front.

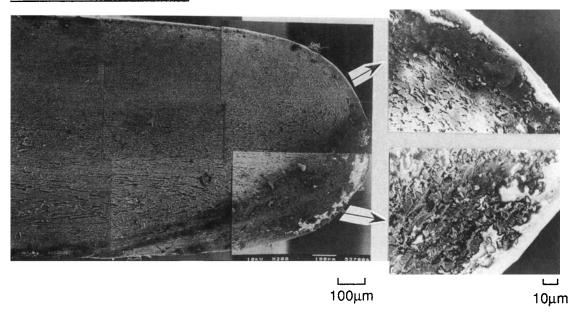
Figure 9 indicates SEM micrographs of the gate region of both articles. In the case of the flow mark article, both PC and ABS flow towards the lower side direction of the mold cavity, whereas in the case of no flow mark article, the PC and the ABS flow straight in the mold cavity. These SEM micrographs shown in Figure 10 are cross-section morphology of both the flow mark article and no flow mark article at several observed area. The PC phase is winding at every part, such as near the gate region, internal region, and side region in the flow mark article.

Thus, it was obvious that these winding flows of PC and ABS at the gate caused a flow mark appearance. Above these results, a designing of the gate may be an important factor of the flow mark appearance.

DISCUSSION

The models for the appearance of a flow mark considered from these observation results are indicated in Figure 11. In the case of a flow mark article, the PC and ABS flow with winding. As a result, the center of the flow front goes towards the mold thickness direction. Such an abnormal fountain flow may be caused by high viscosity resin flow. In this case, high shear stress is applied on the PC and ABS. As a result, the PC phase at the tip of the flow front

Flow mark article



No flow mark article

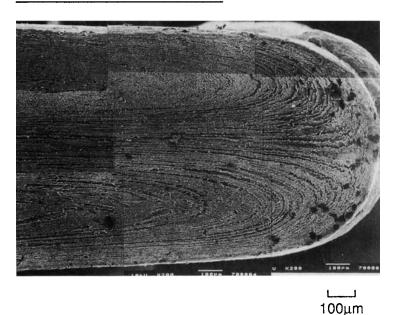


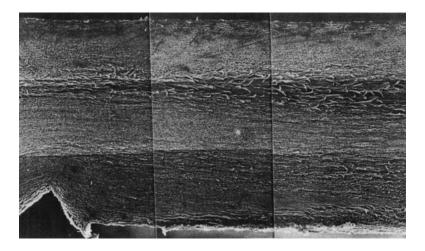
Figure 8 SEM micrographs at the flow front region of the samples.

may be broken, and both PC and ABS coexist. This region flows to the surface of the mold cavity and, thus, become the cloud part. These phenomena are repeated to both the upper and lower side of the surface alternately, and formation of the flow mark is made. On the other hand, in the case of no flow mark article, the PC and ABS flow straight with a

normal fountain flow and are in layers because of its low viscosity. Consequently, the tip of the flow front is covered with PC, and a flow mark does not appear.

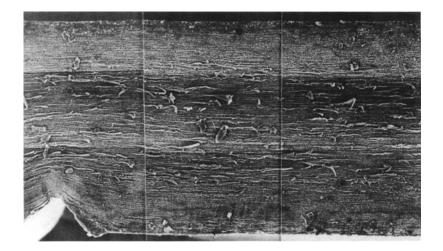
For example, the injection pressure of a flow mark article is 1.2 times higher than that of no flow mark article. Therefore, a flow mark may appear while

Flow mark article



100µm

No flow mark article



100μm

Figure 9 SEM micrographs at the gate region of the samples.

resin is filling from the gate into the mold cavity with high injection pressure, that is to say, with high shear stress at the wall of the gate, so that resin flows with winding from the gate, and this unstable flow, like the melt fracture, causes appearance of a flow mark. Hence, apparent shear rate at the wall of the gate at each injection speed was calculated, and influence of a flow mark appearance was investigated further. The PC/ABS blend is regarded as

the Newtonian flow for simplification. In this case, apparent shear rate at the wall, $\dot{\gamma}_{\rm wa}$, is given by this equation,

$$\dot{\gamma}_{\rm wa} = 6Q/wH^2$$

where Q is the volumetric flow rate, w is the gate width, and H is the gate thickness. The dimensions of the gate that was used in this study were 6 mm

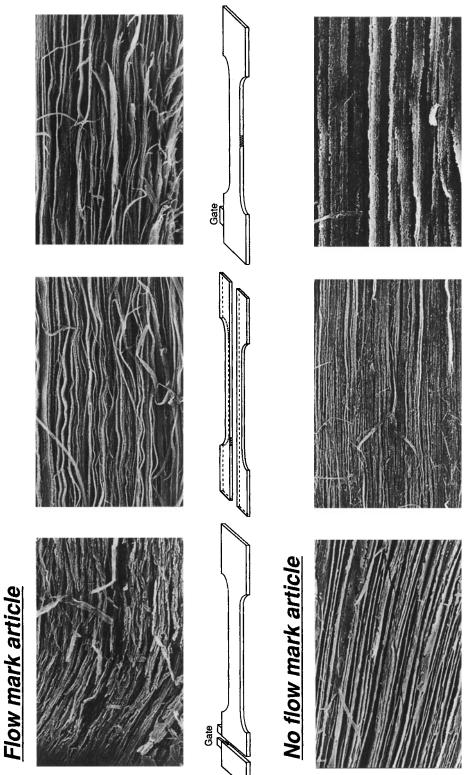
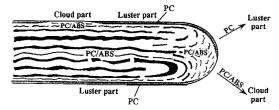


Figure 10 SEM micrographs at various observation areas of the samples.

Flow mark article



No flow mark article

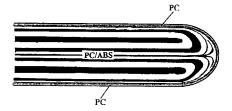


Figure 11 A model for the appearance of a flow mark.

of width and 0.7 mm of thickness. For example, in the case of 300°C of cylinder temperature and 70°C of mold cavity temperature, a flow mark may appear more than $10^5 {\rm s}^{-1}$ of $\dot{\gamma}_{\rm wa}$ from the results as shown in Table II previously. On the other hand, in the case of low cylinder temperature, $\dot{\gamma}_{\rm wa}$ may become higher at each injection speed than in the case of a high cylinder temperature, so that it appears that a flow mark appears at every injection speed, as shown in the table. Therefore, it appears that the appearance of a flow mark can be controlled with lower $\dot{\gamma}_{\rm wa}$, namely, a larger width or thickness of the gate at a high injection speed.

CONCLUSION

The flow mark of PC/ABS blend thin injection moldings was investigated. As a result, the luster part and the cloud part had different structures from analysis of the surface structure. Appearance of a flow mark was concerned with the difference of flow behavior of resin, and the mechanism of a flow mark appearance could be clarified through precise observation of the internal structure. Moreover, designing of the gate is an important factor of a flow mark appearance, and processing conditions that can control the flow mark may be wide by varying the design of the gate.

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