

Skin/ Core Morphology and Tensile Impact Strength of Injection-Molded Polypropylene

INTRODUCTION

In previous papers,¹⁻⁵ we studied the effect of molding conditions and molecular parameters on the skin-core morphology and various mechanical properties of injection-molded polypropylene, and the relationships between the various mechanical properties and the skin-core morphology. In brief, the thickness of the skin layer increased with decreases in cylinder temperature and the melt flow index (MFI) of resin. The tensile yield strength, necking stress, tensile modulus, flexural modulus, flexural strength, mold shrinkage, and annealing shrinkage increased with decreases in the cylinder temperature and MFI and were in linear relationships with the thickness of the skin layer, regardless of the cylinder temperature and MFI. In this paper, we will report the same studies as above about the tensile impact strength (TIS) of injection-molded polypropylene.

EXPERIMENTAL

The polypropylene resins used are shown in Table I. All the samples are commercial isotactic polypropylenes; *M* and *Y* are homopolymers with different MFI, *R* is a random copolymer with ethylene, and *B* is a block-copolymer with ethylene.

The TIS specimens (ASTM D1822) as shown in Figure 1 were injection-molded with a Kawaguchi Churchill 1040S-Type 1.5-oz. reciprocating-screw injection molding machine. Injection molding conditions were as follows: cylinder temperature, cf. Table II; mold temperature, 13°C; cooling time, 10 sec; mold-close pressure, 700 kg/cm²; injection speed, max.; injection pressure, 400 kg/cm² (*M* sample), 500 kg/cm² (*R* and *B* samples), 600 kg/cm² (*Y* sample). The isotropic specimens were obtained by compression molding at 215°C under a pressure of 100 kg/cm² for 10 min, followed by cooling with water.

The molded specimen was cut at the center about 0.1 mm thick in transverse direction, and was observed by a universal projector (Olympus UT350) under cross-nicols with a magnification of 20X.

The TIS was measured at 23°C. The average value of ten samples was adopted.

RESULTS AND DISCUSSION

The polarized micrographs of the cross sections of the TIS specimens are shown in Figure 2; since they were printed by a quick copier, darkness is inverted. Clear two-phase structures with skin (outer bright portion) and core (inner dark portion) are observed in the injection-molded specimens. The skin-core morphology is observed also in the *R* sample, random copolymer with ethylene, and *B* sample, block copolymer with ethylene. The thickness of the skin layer decreases with increasing cylinder temperature. In addition to the skin layer, another oriented layer is observed near the center (like the skin layer, this layer is seen dark under cross-nicols, which means that it is uniaxial with the optical axis of the molded specimen; i.e., in the machine direction, which in turn means that the molecular chains in it orient perpendicular to photograph plane or parallel to the machine direction.

TABLE I
Properties of Samples

Sample name	MFI (dg/min)	Ethylene content (wt. %)	Remarks
<i>M</i>	8.2	0	Homopolymer
<i>Y</i>	1.6	0	Homopolymer
<i>R</i>	4.2	1.8	Random copolymer with ethylene
<i>B</i>	2.7	8.4	Block copolymer with ethylene

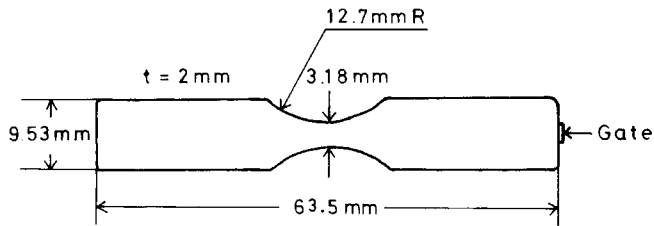


Fig. 1. TIS specimen (ASTM D1822).

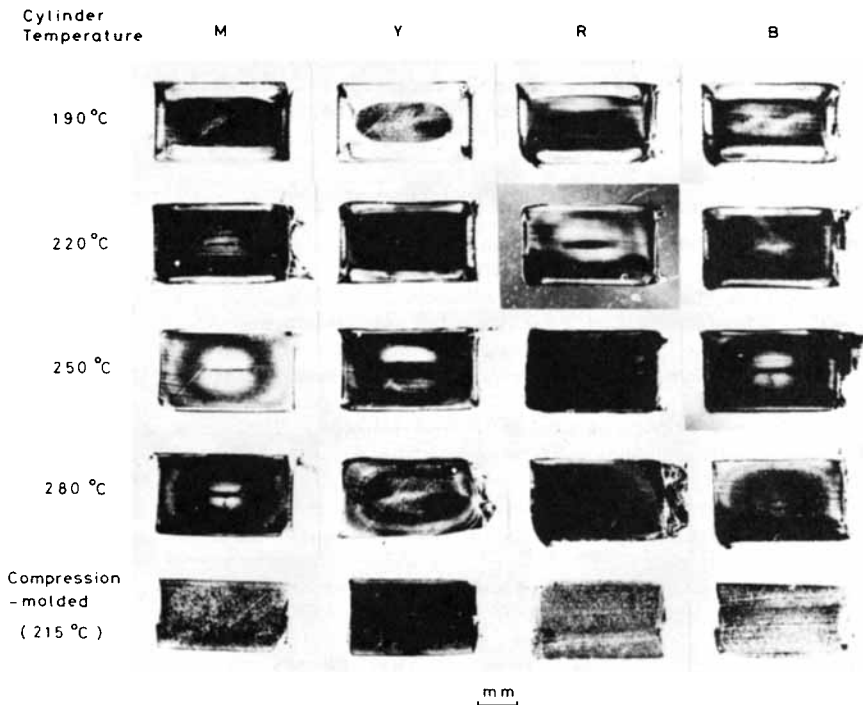


Fig. 2. Variations of the skin-core morphologies with the cylinder temperature.

In a previous paper,⁶ one of us (M.F.) showed that the molecular chains in the skin layer are highly oriented parallel to the machine direction. Since the polypropylenes used are highly crystalline and this layer is cooled more slowly than the skin layer, it cannot be considered that it is amorphous. A similar layer near the center was observed also in an injection-molded ASTM tensile specimen of the *M* sample.² The specimen showed high tensile modulus and yield strength for its thickness of the skin layer. Tan and Kamal⁷ showed from infrared dichroism measurements that the second

TABLE II
Cylinder Temperatures

Exp. No.	MH1 ^a	MH2 ^b	DH ^c Unit (°C)
1	160	190	180
2	190	220	210
3	220	250	240
4	250	280	270

^a Feed, compression zone.

^b Metering zone.

^c Adaptor.

orientation maxima were observed near the center besides the first maxima near the surfaces in an injection-molded linear polyethylene). This layer is most noticeable at the cylinder temperature of 250°C for the *M*, *Y*, and *B* samples, and at 220°C for the *R* sample. It is assumed that this layer might be formed by the second-order flow accompanied with crystallization shrinkage. This layer strongly influence the TIS as shown later.

Next, concerning the quality of the core layer, the spherulites forming the core layer of the injection-molded specimen are finer than those of the compression-molded specimen, though not clear since the photographs are reduced in scale. This is assumed to be due to a severe quenching effect in the injection-molded specimen. The spherulites of the core layer of the *R* sample are finer than those of the others, also though not clear since the photographs are reduced in scale. This is assumed to be due to the lower crystallization temperature of the *R* sample which is a random copolymer with ethylene.

Dependences of the thickness of the skin layer on the cylinder temperature are shown in Figure 3. Comparing the *M* sample and the *Y* sample, the *Y* sample which has lower MFI than the *M* sample shows thicker skin layer than the *M* sample as in previous papers.^{1,2} Although the *R* sample has lower MFI than the *M* sample, it shows thinner skin layer than the *M* sample. This is assumed to be due to the high degree of relaxation of oriented molecular chains in molten state since the *R* sample which is a random copolymer with ethylene shows low crystallization temperature and long crystallization time. The *B* sample, block copolymer with ethylene, also shows thin skin layer (nearly equal to the *M* sample) for its MFI. This might be also due to the low crystallization temperature though not so much as the *R* sample.

Dependences of the TIS's on the cylinder temperature are shown in Figure 4. For comparison, the TIS values of the compression-molded specimens are also shown in Figure 4.

First, we will compare the TIS of the compression-molded specimen among resins. As for homopolymers, the *Y* sample which has lower MFI than the *M* sample shows slightly higher TIS than the *M* sample. The *R* sample which is a random copolymer with ethylene shows slightly higher TIS than the homopolymers. The *B* sample which is a block copolymer with ethylene shows considerably (two to three times) higher TIS than the others. These tendencies coincide with usual common sense. However, the injection-molded specimens show extremely higher TIS than the compression-molded specimens: even homopolymer shows the TIS higher than 100 kg/cm²; in the case of the *R* sample molded at 220°C, the TIS reaches even to 200 kg/cm². In addition, in the injection-molded specimens, the differences among the TIS's of the *M*, *Y*, *R*, and *B* samples, which exist in the compression-molded specimens, diminish, and there are cases where the *R* sample shows higher TIS than the *B* sample. A large increase of the TIS in the injection-molded specimens is assumed to be due to (i) quenching effect which makes the spherulites fine and (ii) orientation effect.

This study was done at the beginning under the viewpoint of the orientation effect, and we expected

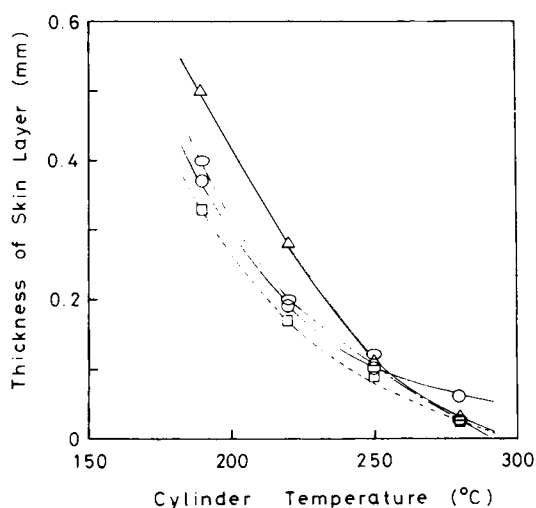


Fig. 3. Dependences of the thickness of the skin layers on the cylinder temperature. \circ , *M*; Δ , *Y*; \square , *R*; \diamond , *B*.

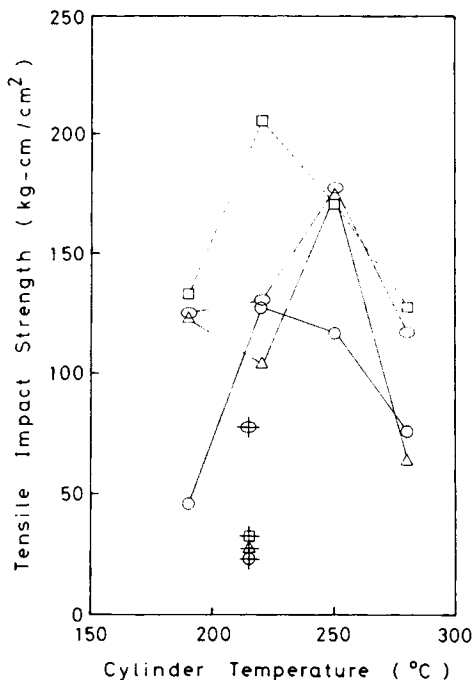


Fig. 4. Dependences of the TIS's on the cylinder temperature. Cross-marked points are for compression-molded articles. \circ , M ; Δ , Y ; \square , R ; \odot , B .

that the lower the cylinder temperature and hence the thicker the skin layer, the higher the TIS. However, as shown in Figure 4, an unexpected result that the TIS shows maxima at the cylinder temperature of 220–250°C was obtained. However, if we compare Figure 4 to Figure 2, we can see that the oriented layer near the center notably appears at the cylinder temperature at which the TIS shows maxima, namely, the fact that the TIS shows maxima originates in the oriented layer besides the skin layer, and hence it may be said that the orientation effect still strongly contributes to high TIS of the injection-molded articles. The injection-molded articles with the oriented layer near the center may be said so-called "steel reinforced" articles. The study to manufacture the "steel reinforced" articles is a left theme.

Next, comparing the R sample and B sample, although the latter shows the TIS more than two times higher than the former in the case of the compression-molded articles, they show nearly equal TIS, or there are even cases where the former shows higher TIS than the latter according to molding conditions in the case of the injection-molded articles. This is, as can be seen from Figure 2, assumed to be due to the quenching effect: the R sample has finer spherulites than the B sample.

From the facts that, in the injection-molded articles, the large difference of the TIS among resins which exists in the compression-molded articles diminishes, and there are cases where the R sample shows higher TIS than the B sample, it is considered that, in the injection-molded articles, the molecular parameters such as molecular weight, molecular weight distribution, tacticity, random and block copolymerizations with ethylene, etc., are considerably suppressed, and the properties are governed mainly by the higher-order structures such as the orientation state of molecular chains, the existence mode of crystalline and amorphous phases, the thickness of lamellae, the orientation state of lamellae, the size of spherulites, etc., and the still higher-order structure such as the existence mode of oriented and nonoriented layers.

CONCLUSIONS

The TIS of polypropylene is improved by injection molding. At the same time, the difference in TIS among resins is reduced. The TIS of injection-molded polypropylene shows a maximum at a cylinder temperature of 220–250°C, at which oriented layers near the center of specimen are notably observed. Since these layers are assumed to be formed by the second-order flow accompanied

with crystallization shrinkage, it is necessary to balance the size of mold gate, hold pressure, and the viscosity and crystallization time of resin to obtain high TIS article.

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