Mutual Interaction between High and Low Stereo-regularity Components for Crystallization and Melting Behaviors of Polypropylene Blend Fibers

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Abstract. Crystallization and melting behaviors of blend fibers of two types of polypropylene (PP), i.e. high stereo-regularity/high molecular weight PP (HPP) and low stereo-regularity/low molecular weight PP (LPP), was investigated. Blend fibers consisting of various HPP/LPP compositions were prepared through the melt spinning process. Differential scanning calorimetry (DSC), temperature modulated DSC (TMDSC) and wide-angle X-ray diffraction (WAXD) analysis were applied for clarifying the crystallization and melting behaviors of individual components. In the DSC measurement of blend fibers with high LPP composition, continuous endothermic heat was detected between the melting peaks of LPP at around 40 °C and that of HPP at around 160 °C. Such endothermic heat was more distinct for the blend fibers with higher LPP composition indicating that the melting of LPP in the heating process was hindered because of the presence of HPP crystals. On the other hand, heat of crystallization was detected at around 90 °C in the case of blend fibers with LPP content of 30 to 70 wt%, indicating that the crystallization of HPP component was taking place during the heating of as-spun blend fibers in the DSC measurement. Through the TMDSC analysis, re-organization of the crystalline structure through the simultaneous melting and re-crystallization was detected in the cases of HPP and blend fibers, whereas re-crystallization was not detected during the melting of LPP fibers. In the WAXD analysis during the heating of fibers, amount of α-form crystal was almost constant up to the melting in the case of single component HPP fibers, whereas there was a distinct increase of the intensity of crystalline reflections from around 100 °C, right after the melting of LPP in the case of blend fibers. These results suggested that the crystallization of HPP in the spinning process as well as during the conditioning process after spinning was hindered by the presence of LPP.

Keywords: polypropylene, melt spinning, crystallization, stereo-regularity

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INTRODUCTION

In recent years, development of metallocene catalysts enabled us to control the molecular weight distribution and composition distribution of polypropylenes (PP), which attracts much attention from the view point of higher order structure control. Especially, low stereo-regularity PP (LPP) prepared with such technology has the characteristics of low crystallinity, low crystallization rate and elastomeric properties. In the market, newly commercialized LPP is being used either as the resin modifier for improving processability of high stereo-regularity PP (HPP) or as the major component for producing elastomeric nonwoven fabrics through the spunbonding process. In the latter case, LPP is normally blended with HPP to avoid the sticking of fibers each other.

We have reported the effect of the addition of LPP in the melt spinning of HPP, and confirmed the improvements of processability and mechanical properties. High crystallinity despite of relatively high LPP content was considered to be the origin of high tensile modulus [1]. Regarding the development of elastomeric fibers of LPP, we have also investigated the bicomponent spinning of sheath-core fibers with HPP/LPP blend as the sheath component and pure LPP as the core component, and found that the crystallinity of both HPP and LPP decreased with the increase of sheath layer composition [2]. Even after detailed analysis of the structure of resultant as-spun fibers, however, exact mechanisms either for the improvement of spinnability nor for the variations of fiber structure formation behavior in the HPP/LPP blend has not been clarified yet.
In this study, blend fibers of wide range of HPP/LPP compositions were prepared by the melt spinning process, and the mechanism of fiber structure formation accompanied by the crystallization of individual components was investigated through the detailed thermal analysis of as-spun fibers. Particular attention was paid for the effect of mutual interaction between two components of different stereo-regularities on the crystallization behavior of each component.

**EXPERIMENTAL**

The materials used in this study were two types of polypropylenes, i.e. high stereo-regularity/high molecular weight PP (HPP, $T_m = 161.0 \, ^\circ\text{C}$, MFR = 20 g/10min) and low stereo-regularity/low molecular weight PP (LPP, $T_m = 59.6 \, ^\circ\text{C}$, MFR = 60 g/10min). Single component fibers of HPP and LPP and blend fibers with HPP/LPP compositions of 5:95, 10:90, 15:85, 30:70, 50:50, 60:40, 70:30, 80:20 and 90:10 wt% were prepared through the melt spinning process. Dry-blended polymer pellets were melted and extruded through a single screw extruder, metering pump and a single-hole spinneret of diameter 1.0 mm. The through-put rate and extrusion temperature were set at 6 g/min and 200 °C, respectively. The prepared blend fibers with different HPP/LPP compositions were designated as HLxy with x and y representing the weight percent of HPP and LPP, respectively. Differential scanning calorimetry (DSC), temperature modulated DSC (TMDSC) and wide-angle X-ray diffraction (WAXD) measurements were carried out in the heating process to analyze the melting and crystallization behaviors in the as-spun fibers.

**RESULTS AND DISCUSSION**

*Melting Behavior*

DSC thermograms of LPP, HPP/LPP blend and HPP fibers measured at the heating rate of 10 °C/min are shown in FIGURE 1. The LPP fiber showed double melting peaks at around 40 and 60 °C, whereas the HPP fiber showed a single melting peak at around 160 °C. In the case of blend fibers with high LPP composition, continuous endothermic heat was detected between the melting peaks of LPP and HPP. Such endotherm in the intermediate temperature range was more distinct for the blend fibers with higher LPP content, indicating that the melting of LPP in the heating process was hindered by the presence of HPP. On the other hand, in the case of blend fibers with LPP content of 30 to 70 wt%, heat of crystallization was detected at around 90 °C, indicating that there was a crystallization of HPP component during the heating of blend fibers.

![FIGURE 1. DSC heating thermograms of LPP, HPP/LPP blend and HPP fibers. Take-up velocity 1 km/min.](image)

TMDSC measurement was carried out at a heating rate of 3 °C/min under the heat only mode with the period and amplitude of temperature modulation of 60 s and ±0.48 °C, respectively. TMDSC thermograms of LPP, HL1585, HL5050 and HPP fibers obtained at the take-up velocity of 1 km/min are shown in FIGURE 2. The total heat flow (Total, blue line) was separated into non-reversing heat flow (Non-Rev., green line) and reversing heat flow (Rev., red line).
red line). In general, non-reversing heat flow represents the slow phenomena such as crystallization, and reversing heat flow represents the fast phenomena such as melting of small crystallites. In the case of HPP, melting appeared to start at around 140 °C in the total heat flow. However, reversing heat flow showed the endothermic heat of melting from around 90 °C, whereas non-reversing heat flow showed the exothermic heat of crystallization from around 90 °C. These results indicated that the structural re-organization (simultaneous melting and re-crystallization) started to occur from about 90 °C even though there was no sign of structural change in the total heat flow. On the other hand, exothermic heat did not appear in the case of LPP indicating re-organization did not occur in this heating condition. In the case of blend fibers, melting of LPP and HPP as well as the continuous re-crystallization of HPP between the melting of LPP and HPP were detected in the reversing and non-reversing heat flows.

![TMDSC thermograms of LPP, HL1585, HL5050 and HPP fibers. Take-up velocity 1 km/min.](image)

**Structural Changes during Heating**

WAXD measurement was carried out in the heating process of as-spun fibers at a heating rate of 2 °C/min. The WAXD patterns for LPP, HL1585, HL5050 and HPP fibers obtained at various temperatures are shown in FIGURE 3. The LPP fibers showed the structure with α-form crystal of no orientation. With the increase of temperature, intensity of crystalline reflections started to decrease from around 30 °C. The HPP fibers showed the bimodal orientation with the orientation of c- and a*-axis in the α-form crystals along the fiber axis. In the case of HL1585 and HL5050 blend fibers, distinct crystalline reflections of highly oriented α-form crystal of c-axis orientation started to appear on the equator at elevated temperatures of around 100 °C.

Variations of the equatorial WAXD intensity profiles with increasing temperature for the HPP and HL5050 fibers are shown in FIGURE 4. In the case of HPP, intensity of (040) reflection which can be assigned to both c- and a*-axis oriented crystals did not change upon heating, whereas the intensity of the equatorial reflections of (110) and (130) increased with increasing temperature indicating the reduction and increase of a*-axis and c-axis oriented crystals, respectively. In the case of HL5050, intensities of (110), (040) and (130) reflections started to increase from...
around 100 °C. These results suggested that the crystallization of HPP in the spinning process as well as during the conditioning process after spinning was hindered by the presence of LPP, and the crystallization of HPP started to occur during the heating of as-spun fibers after the melting of LPP crystals. These results of WAXD analyses are in accordance with the results of DSC and TMDSC thermograms.

![WAXD images of LPP, blend and HPP fibers at selected temperatures. Take-up velocity 1 km/min.](image1)

**FIGURE 3.** WAXD images of LPP, blend and HPP fibers at selected temperatures. Take-up velocity 1 km/min.

![Equatorial WAXD intensity profiles of (a) HPP 1 km/min and (b) HL5050 1 km/min](image2)

**FIGURE 4.** Equatorial WAXD intensity profiles of (a) HPP 1 km/min and (b) HL5050 1 km/min

**CONCLUSIONS**

Mutual interaction of the HPP and LPP components in the HPP/LPP blend fibers was investigated from the viewpoint of crystallization and melting behaviors. Through the DSC and TMDSC measurements, it was found that the melting of LPP component was hindered by the presence of HPP crystals in the heating process of as-spun fibers, whereas crystallization of HPP component in the spinning process as well as during the conditioning process after spinning was hindered by the presence of LPP.

**REFERENCES**