Structure and properties of low-isotacticity polypropylene elastomeric fibers prepared by sheath-core bicomponent spinning: effect of localization of high-isotacticity component near the fiber surface

Abstract: Sheath-core type bicomponent melt-spun fibers were produced by extruding the melts of low-isotacticity polypropylene (LPP) as the core component and the blend of LPP and high-isotacticity PP (IPP) as the sheath component. IPP content in the sheath was changed from 8 wt% to 40 wt% while sheath/core composition was varied from 50/50 to 10/90. Accordingly overall IPP content was kept constant at 4 wt%. Even though the overall IPP content was intact, bicomponent fibers with lower contraction ratio after spinning, higher elastic recovery and slightly higher modulus and strength were obtained by increasing the IPP content in the sheath and decreasing the sheath layer composition, i.e., localizing the IPP to the region near the surface in the fiber cross-section. Structure analysis of the as-spun fibers suggested the suppression of crystallization of LPP in the sheath by blending IPP. By contrast, enhancement of molecular orientation and crystallization of the sheath component were found to occur by localizing the IPP to the region near the fiber surface. It was speculated that this behavior was caused by the kinematic mutual interaction of the sheath and core components in the melt spinning process.

Keywords: bicomponent fiber; elastic recovery; elastomeric fiber; isotacticity; polypropylene.

1 Introduction

Polypropylene (PP) has been widely used commercially for the production of fibers, non-woven fabrics, films, injection-molded products, etc. For the production of PP, introduction of metallocene catalysts provided the technologies for designing new types of polymers [1–7], and recently, development of low-isotacticity PP (LPP) with elastomeric characteristics was achieved. Structure and properties of such PP have been investigated widely because of its unique characteristics [8–13]. It was reported that the modification high-order structure and physical properties, as well as the improvement of processability of conventional high-isotacticity PP (IPP), was possible by blending a small amount of elastomeric PP [14–17]. By contrast, a technology for producing non-woven elastomeric fabrics has been developed recently by applying the spun-bonding process to the elastomeric PP [18]. Improvement of the production of non-woven fabrics achieving a good balance of processability and elastomeric recoverability of the product has been attempted by introducing the sheath-core bicomponent melt spinning process [19–22].

In a previous paper, we investigated the effects of sheath/core composition on the high-order structure and mechanical properties of elastomeric bicomponent fibers consisting of LPP as the core component and the blend of LPP and IPP as the sheath component, in that the sheath layer composition and the total IPP content were varied, while keeping the IPP content in the sheath layer constant at 10 wt% [23]. Through the analyses of the as-spun bicomponent fibers, it was found that the as-spun fibers exhibit a relatively large elastic recovery of higher than 85%, and that the crystallization of IPP was enhanced when the sheath layer composition was low, while the crystallization of LPP was suppressed with the increase in the sheath layer composition.
In this research, with the aim of producing LPP fibers of high elastic recoverability while keeping the overall IPP content constant, various sheath-core fibers consisting of LPP as the core component and the blend of LPP and IPP as the sheath component were produced, and high-order structure and elastomeric properties of the as-spun sheath-core bicomponent fibers were investigated.

2 Materials and methods

2.1 Materials

A new fiber and non-woven grade LPP commercialized in 2012 (LPP; L-MODU, S901, Idemitsu Kosan Co., Ltd., Chiba, Japan) was used in this study. The polymer was produced through the polymerization process applying a double cross-linked metallocene catalyst. For the improvement of the crystallizability of LPP, isotactic PP (IPP, Y6005GM, Prime Polymer Co., Ltd., Chiba, Japan) was blended to LPP. Properties of the polymers used in this study are listed in Table 1. The melts of both polymers have similar viscosity. LPP has an extremely low melting temperature of 70°C because of its low isotacticity.

2.2 Melt spinning of bicomponent fibers

Sheath-core type bicomponent fibers were produced by extruding the melts of the blend of LPP and IPP as the sheath component and LPP as the core component using two extrusion systems, each of which consisted of a single screw extruder and a metering pump. The spinneret had eight spinning holes of 0.5 mm diameter. The extrusion temperature and throughput rate were set at 220°C and 1.0 g/min/hole, respectively. Fiber samples were prepared at the take-up velocity of 2 km/min. In a previous paper, sheath IPP content was kept constant at 10 wt% while sheath layer composition was varied from 0% to 50% [23]. Accordingly, total IPP content was changed from 0 wt% to 5 wt%. By contrast, in this series of experiments, IPP content in the sheath was set from 8 wt% to 40 wt%, while the sheath/core composition was varied from 50/50 to 10/90. Accordingly, the overall IPP content was kept constant at 4 wt%. Sheath layer composition, sheath IPP content and total IPP content are summarized in Table 2.

Since the as-spun fibers have a relatively low tensile modulus, the spin-line tension causes the elastic stretching of the fiber in the spin-line before the fibers are wound up on the bobbin. Therefore, when the fibers were cut off from the bobbin after the spinning, contraction of the fibers to the original length was observed. The contraction ratio was calculated from the circumference length of the bobbin, \(L\), and the length of cut-off fiber samples, \(R\), using the following equation [Eq. (1)]:

\[
\text{Contraction Ratio (\%)} = \frac{L - R}{L} \times 100
\]

2.3 Evaluation of elastic recovery

Elastic recovery measurements were conducted for the as-spun fibers using a tensile testing machine (Shimadzu Corporation, Autograph AG-I). The gauge length \(L_0\) was 50 mm, and the cross-head speed for extension and recovery were 150 mm/min. In the measurement, the fibers were firstly stretched to strain 100%. Secondly, the cross-head was returned to the initial position. At this moment, the stress was zero because of the incorporation of permanent extension after the first stretching. Finally, the cross-head was moved for the second stretching, and the position \(L\) where the stress started to appear again was measured. The elastic recovery was calculated by using the following equation [Eq. (2)]:

<table>
<thead>
<tr>
<th>Sheath layer composition (wt%)</th>
<th>Sheath IPP content (wt%)</th>
<th>Overall IPP content (wt%)</th>
</tr>
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<tbody>
<tr>
<td>10</td>
<td>40</td>
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<td>4</td>
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<td>50</td>
<td>8</td>
<td>4</td>
</tr>
</tbody>
</table>

Note: Sheet sample for differential scanning calorimetry (DSC) analysis was prepared as follows: compression molding of the polymer at 220°C, quenching in water, and conditioning at room temperature for more than 1 week.

MFR, melt flow rate.
2.4 Tensile test

The load-elongation curves of the as-spun fibers were obtained using the same tensile testing machine for the elastic recovery measurement. The gauge length and tensile speed were 50 mm and 150 mm/min, respectively. The tensile modulus, the tensile strength and the elongation at break were obtained averaging at least 10 trials of the tensile test for each sample.

\[
\text{Elastic Recovery (\%) = } \left(1 - \frac{L}{L_0}\right) \times 100
\]

(2)

2.5 Wide angle X-ray diffraction measurement

Wide angle X-ray diffraction (WAXD) patterns of the as-spun fibers were obtained using an X-ray generator and a charge-coupled device (CCD) camera (Rigaku Denki, RTM-18HFVE, CCD Mercury). The generator was operated at 45 kV and 60 mA, and the WAXD patterns of the fiber bundle were taken at the exposure condition of five times/10 s.

2.6 Birefringence measurement

Birefringence of as-spun fibers was analyzed through the measurements of fiber diameter and optical retardation using a polarizing optical microscope (Olympus, BH-2) equipped with a Berek compensator. Since the measurement was performed at the center of the fiber, the obtained overall birefringence represents the mean value of sheath and core components averaged along the diameter. Thus, in comparison with the averaging based on the weight fractions of both components, there can be a slightly enhanced contribution of the core component.

2.7 Differential scanning calorimetry measurement

Thermal analysis of the as-spun fibers was performed with a differential scanning calorimeter (DSC) (Perkin Elmer, DSC 8500) equipped with a liquid nitrogen cooling system for the measurements from low temperature. The measurement was conducted from -40°C to 220°C at a heating rate of 10°C/min.

The crystallinity of pure IPP and LPP, \(X_{c,IPP}\) and \(X_{c,LPP}\), were calculated by using the following equations [Eqs. (3) and (4)], where \(\Delta H_{IPP}\) and \(\Delta H_{LPP}\) are the heat of fusion of IPP and LPP, and \(W_{IPP}\) and \(W_{LPP}\) are the weight fractions of the IPP and LPP components. The heat of fusion for PP with 100% crystallinity, \(\Delta H^*\), was assumed to be 209 J/g [24]:

\[
X_{c,IPP} (%) = \frac{\Delta H_{IPP}}{\Delta H^* W_{IPP}} \times 100
\]

(3)

\[
X_{c,LPP} (%) = \frac{\Delta H_{LPP}}{\Delta H^* W_{LPP}} \times 100
\]

(4)

3 Results and discussion

3.1 Melt spinning behavior

The contraction ratio of the fiber length after spinning was plotted against the sheath layer composition in Figure 1. IPP content in the sheath layer is also indicated in the figure. The contraction ratio decreased continuously from 12% to 2% with the decrease of sheath layer composition from 50% to 10% and the increase of IPP content in the sheath from 8% to 40%. In other words, a reduction of the contraction ratio with the constant IPP content was achieved by localizing the IPP to the region near the fiber surface in the fiber cross-section.

![Figure 1 Variation of contraction of as-spun high-isotacticity polypropylene (IPP)/low-isotacticity PP (LPP) bicomponent fibers after spinning with sheath IPP content and sheath layer composition.](image-url)
3.2 Mechanical properties of as-spun fibers

Stress-strain hysteresis curves for the multiple cycles of stretching and recovery of as-spun fibers with the sheath IPP content of 40 wt% and 8 wt%, which correspond to the sheath layer compositions of 10% and 50%, respectively, are compared in Figure 2. There was a significant change in the stress-strain behavior between the first and second stretchings, whereas almost identical behaviors were observed for the second and the third stretchings. A certain level of hysteresis was observed between the stretching and recovery even after the second stretching. By localizing the IPP to the region near the fiber surface, the overall stress level during the first stretching increased significantly, while reduction of the stress level from the first to the second stretching was more significant.

Variation of elastic recovery after the first stretching with the increase of sheath layer composition is shown in Figure 3. All samples showed a fairly high elastic recovery of higher than 85%, while there was an improvement of elastic recovery with the reduction of the sheath layer composition and the increase of sheath IPP content.

Tensile modulus of the as-spun fibers is plotted against the sheath layer composition in Figure 4. The tensile modulus decreased with the increase in the sheath layer composition and with the decrease of sheath IPP content. In a previous paper [23], it was found that there was a quantitative accordance between the variation of contraction ratio after spinning and the variation of tensile modulus of the as-spun fibers with the change of sheath layer composition. This was because the higher tensile modulus corresponded to the lower degree of elastic stretching in the spin-line. In this research, however, the contraction ratio significantly decreased from 12% to about 1%–2% when the sheath layer composition was decreased from 50% to 10%, while the increase in the tensile modulus of fibers with the increase of sheath IPP content was only about 25% (from 80 MPa to 100 MPa). The reason for
such a discrepancy is not clear at the moment. To explain the extremely low contraction ratio of the fibers with the sheath layer compositions of 10 wt% and 20 wt% in comparison with the tensile moduli of those fibers, progress of structural change possibly accompanied by the crystallization needs to occur either in the sheath or core components after the fiber was wound up on the bobbin.

By contrast, to clarify the origin of the different characteristics between the fibers with different sheath layer compositions, the tensile modulus of the sheath component was estimated based on a simple parallel model, assuming the constant tensile modulus of 38 MPa for the core component, which corresponds to that of the pure LPP single component fiber. The estimated tensile modulus of the sheath component increased from 113 MPa to 667 MPa with the decrease of sheath layer composition as shown in Figure 5.

Increasing tendency of the tensile modulus with the decrease of sheath layer composition can be regarded as a normal behavior, since the IPP content increases at the same time, however it should be noted that there can be another mechanism for the increase in the tensile modulus of sheath component. As described in a previous paper [25, 26], when the sheath layer composition is decreased, its structure development behavior can be altered significantly in comparison with its single component spinning, because of the kinetic mutual interaction of the sheath and core components in the melt spinning process of bicomponent fibers. In the bicomponent melt spinning of the LPP and the blend of IPP and LPP, enhancement of the structure formation of the blend can be expected because of its higher crystallizability. Such an effect becomes more significant for the sheath or core component with lower composition [23].

Tenacity and elongation at break of the as-spun fibers are plotted against sheath layer composition in Figures 6 and 7. The tensile strength increased, whereas the elongation at break decreased with the decrease of sheath layer composition, that is, by localizing the IPP to the region near the fiber surface.

Summarizing the above, it was found that even though the total IPP content was kept constant, the contraction ratio after spinning became lower, and the as-spun fibers with higher elastic recovery, slightly higher modulus and strength, and lower elongation were obtained by the enhanced localization of IPP component in the cross-section of LPP fiber.
3.3 Fiber structure

WAXD patterns of the as-spun fibers of various sheath layer compositions are shown in Figure 8. All as-spun fibers showed similar WAXD patterns with highly oriented α form crystals. Effects of sheath/core composition and IPP content in the sheath were not clear.

In our previous study on the sheath-core bicomponent spinning of IPP and LPP, the IPP component showed highly oriented α form crystals, whereas the LPP component showed α form crystals of virtually no orientation [27]. The mechanism for the development of such structure was speculated as follows. In the bicomponent spin-line, crystallization of the IPP component proceeded at a relatively high temperature before the starting of the crystallization of LPP. This caused the termination of the spin-line thinning and thus the orientation relaxation of the LPP component. In this study, however, by changing the sheath layer component from pure IPP to the blend of IPP and LPP, both sheath and core components showed high crystalline orientation.

By contrast, in our previous paper on the sheath-core bicomponent melt spinning of the blend of IPP and LPP with the constant IPP content of 10 wt% as the sheath and the pure LPP as the core [23], it was speculated for the mechanism of the formation of highly oriented α form crystals in the core that even though crystallization of the IPP component in the blend started to occur at higher temperatures, deformability of the blend could be maintained because the content of IPP was only 10 wt%, and accordingly orientation of the core component, LPP, could proceed in the spin-line. In this research, highly oriented α form crystals were formed in the core even when the IPP content in the blend was increased up to 40 wt%, suggesting that the deformability of the blend of IPP and LPP was maintained after starting the crystallization of the IPP component in the spin-line, even at such a high IPP content.

Variation of overall birefringence of as-spun fibers with sheath layer composition and the sheath IPP content is shown in Figure 9. All as-spun fibers exhibited similar levels of birefringence. This is partly because the measured birefringence in this research represents the averaged birefringence of the sheath and core components.

Considering the above, birefringence of the sheath component was estimated assuming the birefringence of the core component LPP to be $9.9 \times 10^{-3}$, which corresponds to the birefringence of the as-spun single component LPP fiber prepared at the same take-up velocity. The detailed calculation method was reported in a previous paper [23].

Birefringence of the sheath component estimated through the method stated above is plotted against the sheath layer composition and the sheath IPP content as shown in Figure 10. When the sheath layer composition was 50 wt%, no boundary between the sheath and the core could be observed under the polarizing microscope. This fact is consistent with the result in Figure 10 that the sheath and core have a similar level of birefringence at this composition.

Figure 8 Wide-angle X-ray diffraction patterns of as-spun high-isotacticity polypropylene (IPP)/low-isotacticity PP (LPP) bicomponent fibers of five different sheath layer compositions.
By contrast, birefringence of the sheath component increased with the increase in IPP content in the sheath layer and also with the decrease in the sheath layer composition. Increase of birefringence in the sheath layer with the increase of IPP content can be expected, however, estimated birefringence of 40×10⁻³ is significantly higher than that of single-component IPP fiber prepared at the same take-up velocity. This result is further evidence for the enhanced structure formation in the sheath component when the sheath layer composition was as low as 10%, which was discussed for the estimated tensile modulus of the sheath component in Figure 5.

It should be noted that assumption of the birefringence of the core to be similar to that for the single component LPP fiber is reasonable because: (1) if the sheath composition is only 10%, melt spinning behavior is governed by the core component; and (2) even if there is an effect of the kinematic mutual interaction between the sheath and core components, it leads to the reduction of the birefringence of the core component, which yields further increase of the estimated birefringence of the sheath component.

DSC curves of as-spun fibers are shown in Figure 11. Melting peaks of the LPP and IPP components were detected at 50°C–80°C and at around 165°C, respectively. The melting peak of LPP consisted of two peaks, a relatively sharp peak at a lower temperature of around 50°C and a relatively broad peak at a higher temperature of around 75°C. Even though total IPP content was constant, different behaviors were observed for the melting of LPP depending on the LPP composition in the sheath. Particularly, with the decrease of sheath layer composition, peak height of the lower temperature peak tended to decrease in comparison with the peak area of the higher temperature peak of 75°C.

The melting behavior of the as-spun fibers was analyzed through DSC. Figure 12 shows the variations of the melting enthalpies of IPP and LPP as well as the total melting enthalpy with the changes in the sheath layer composition and the sheath IPP content. Even though the total IPP content was kept constant, total melting...
enthalpy for IPP increased by localizing the IPP near to the fiber surface. By contrast, the melting enthalpy for LPP decreased with the increase of sheath layer composition.

If constant crystallinity of pure LPP in the core is assumed, this result indicates that the crystallization of LPP was suppressed by blending IPP. This behavior is similar to the one observed in a previous paper [23]. By contrast, a slight increase of the IPP melting peak area may indicate that a small amount of LPP molecules are incorporated into the IPP crystals.

### 3.4 Mechanism of structure formation in sheath-core fibers

Gathering the experimental results stated above, the mechanism of fiber structure development in the bicomponent melt spinning of the LPP and the blend of IPP and LPP can be summarized as follows. Firstly, when the sheath layer composition is 50 wt%, the spinning behavior and structure formation in both sheath and core components were considered to be similar to those for the single component fiber of pure LPP. With the decrease of the sheath layer composition, crystallinity and molecular orientation in the sheath were expected to increase because of the increased content of IPP. In addition, from the view point of the kinematic mutual interaction of the sheath and core components in the melt spinning process, structure development of the sheath was expected to be enhanced with the decrease in the sheath layer composition. The reasons for such prediction are that: (1) the kinematic mutual interaction of the sheath and core components in the spinning process on the structure development is more effective to the component with lower composition; and (2) the structure development of the component with higher IPP content should be enhanced more effectively because a larger difference in thinning behavior in the single component melt spinning process in comparison with that for the pure LPP can be expected because of its higher crystallizability.

### 4 Conclusions

In the bicomponent melt-spinning of sheath-core fibers, LPP and the blend of LPP and IPP were used as the core and sheath components, where IPP content in the sheath was changed from 8 wt% to 40 wt% and the sheath/core composition was varied from 50/50 to 10/90. Even though the total IPP content was kept constant at 4 wt%, the bicomponent fibers with lower contraction ratio after spinning, higher elastic recovery and slightly higher modulus and strength were obtained by localizing IPP to the region near the surface in the fiber cross-section. Structure analysis of the as-spun fibers suggested that there was a suppression of the crystallization of LPP by blending IPP, whereas the molecular orientation and crystallization of the sheath component was enhanced by localizing the IPP near to the fiber surface because of the kinematic mutual interaction of the sheath and core components in the bicomponent melt spinning process.

### References


