**Structure and Properties of Low-Isotacticity Polypropylene Elastomeric Fibers Prepared
by Sheath-Core Bicomponent Spinning
- Effect of the Composition of Sheath Layer with Constant
High-Isotacticity Polypropylene Content -**

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Abstract: Development of metallocene catalyst provided the technologies for producing new types of polyethylene (PE) and polypropylene (PP). Based on this technology, PPs with controlled low-isotacticity (LPP) has been developed and applied for the production of elastomeric fibers. However, difficulty arose in the spun-bonding process of non-woven fabrics consisting of the LPP fibers because of its low crystallizability. With the aim of improving the processability, melt spinning of sheath-core type bicomponent fibers was performed in this research using the blend of LPP and ordinary high-isotacticity polypropylene (IPP) as the sheath component and pure LPP as the core component. The prepared as-spun fibers with IPP content of 10 wt% in the sheath showed elastomeric property with reasonably good elastic recovery of higher than 85 wt%. The elastic recovery showed slight reduction with the increase of sheath layer composition from 0 to 50 wt%, which corresponds to the increase of total IPP content from 0 to 5 wt%. Tensile modulus and tensile strength of the as-spun bicomponent fibers increased significantly with the increase of total IPP content. Structural analyses of as-spun fibers consisting of LPP and IPP revealed that the crystallization of IPP component was enhanced especially when the composition of sheath component was low while that of LPP was suppressed significantly with the increase of the total IPP content. These results suggested the high modulus of sheath component in the fibers with low sheath layer composition.

Keywords: Elastic fiber ; Bicomponent spinning ; Elastic recovery ; Polypropylene ; Isotacticity

(Received 2 June, 2014 ; Accepted 23 June, 2014)

1. Introduction

Polyolefines such as polyethylene (PE) and polypropylene (PP) are widely used for the production of fibers, non-woven fabrics, films, injection-molded products etc. Conventionally, PE and PP have been polymerized applying Ziegler-Natta catalyst. Development of metallocene catalyst provided the technologies for designing new types of polymers such as those with narrow molecular weight and composition distributions, controlled stereo regularity [1-2], copolymerization [3-7] etc. Especially, development of polymers with elastomeric characteristics is widely investigated recently [8-13]. Elastomeric fibers and elastomeric non-woven fabrics produced from such

polyolefin elastomers can be applied widely for the production of diapers, sanitary goods, hygiene products, and materials for medical uses. Optimized elastomeric properties and recoverability are required for the production of disposable diapers and sanitary products since these products contacts directly with human body.

A technology for producing non-woven elastomeric fabrics through the spun-bonding process applying the PP of low stereo regularity (LPP) with uniformly controlled composition distribution has been under development. Since the crystallization rate of low stereo regularity PP is low, troubles of the adhesion and wrapping of non-woven fabrics to the embossing roll occurs frequently. Such troubles could be eliminated by enhancing the crystallization rate through the addition of a small amount of high stereo regularity PP to the LPP, however there was a certain level of the deterioration of elastic

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recoverability [14]. Accordingly, investigations for producing non-woven fabrics with balanced processability and elastomeric recoverability has been conducted by applying sheath-core bicomponent spinning process, in that LPP blended with the high stereo regularity PP (IPP) is used for the sheath component [15-18]. In this research, as one of the series of researches on bicomponent fibers of LPP and IPP, effects of sheath/core composition on the high-order structure and physical properties of elastomeric fibers consisting of IPP/LPP blend as the sheath component and pure LPP as the core component were investigated keeping the LPP content in the sheath constant at 10 wt%.

2. Experimental

2.1 Materials

A low-isotacticity polypropylene for fibers and non-wovens applications commercialized in 2012 (LPP; L-MODU™, S901, Idemitsu Kosan Co., Ltd.) was used in this study. This polymer was polymerized applying a double cross-linked metallocene catalyst. For the improvement of the crystallizability of LPP, 10 wt% of ordinary isotactic polypropylene (IPP, Y6005GM, Prime Polymer Co., Ltd.) was blended to LPP. Properties of the polymers used are listed in Table 1. The melts of both polymers have similar flowability. Because of the low-isotacticity, LPP has extremely low melting temperature of 70 °C.

2.2 Melt spinning of bicomponent fibers

Sheath-core type bicomponent fibers were produced by extruding the melts of LPP/IPP blend as the sheath component and LPP as the core component using two extrusion systems, each of which is consisting of a single screw extruder and a metering pump. The spinneret has eight spinning holes of 0.5 mm diameter. 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. This take-up velocity corresponds to the spinning velocity attained in the ordinary spun-bonding process. In this series of experiment, IPP content in the sheath was set at 10 wt% while sheath/core composition was varied from 10/90 to 50/50. Accordingly overall IPP content varied from 1 to 5 wt%. Sheath/core composition and overall IPP content are summarized in Table 2.

Since the as-spun fibers are elastomeric and have 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 (1).

$$\text{Contraction Ratio (\%)} = \frac{L - R}{L} \times 100 \quad (1)$$

Table 1 Characteristics of low- and high-isotacticity polypropylenes, LPP and IPP.

	M_w	M_w / M_n	MFR (g/10min)	T_m (°C)	ΔH (J/g)	X_c (%)
LPP	1.2×10^5	2.0	60	70	27	13
IPP	1.6×10^5	3.7	60	165	90	43

Notes : Sheet sample for 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.

Table 2 Sheath/core composition and overall IPP content of as-spun IPP/LPP bicomponent fibers.

Sheath layer composition (wt%)	Sheath IPP content (wt%)	Overall IPP content (wt%)
0	-	0
10	10	1
20	10	2
30	10	3
40	10	4
50	10	5

2.3 Observation of the fiber cross-section

To confirm the formation of desired cross-sectional configuration, some fiber samples were prepared using the sheath component colored with a master batch pellet containing a small amount of carbon black. The cross-section of thus prepared fiber samples was observed with a transmission electron microscope (JEOL, TEM JEM-2100).

2.4 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 stress was zero because of the incorporation of permanent extension to the fiber sample 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 (2).

$$\text{Elastic Recovery (\%)} = \left(1 - \frac{L}{L_0}\right) \times 100 \quad (2)$$

2.5 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 ten trials of the tensile test for each sample.

2.6 Wide angle X-ray diffraction (WAXD) measurement

Wide angle X-ray diffraction (WAXD) patterns of the as-spun fibers were obtained using an X-ray generator and a CCD camera (Rigaku Denki, RTM-18HFVE, CCD MERCURY). The generator was operated at 45 kV and 60 mA, and the WAXD patterns of fiber bundle were taken at the exposure condition of 5 times/10 s.

2.7 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. In comparison with the averaging based on the weight fractions of both components, there can be a slightly enhanced contribution of the core component for the obtained birefringence value.

2.8 Differential scanning calorimetry (DSC) measurement

Thermal analysis of the as-spun fibers was performed with a DSC (PERKIN ELMER, DSC 8500) equipped with a liquid nitrogen cooling system for the measurements from a temperature lower than the room temperature. The measurement was conducted from -40 to 220 °C at a heating rate of 10 K/min.

Crystallinity of pure IPP and LPP, X_{c-IPP} and X_{c-LPP} were calculated by using the following equations (3) and (4), where ΔH_{IPP} and ΔH_{LPP} are the heat of fusion, and W_{IPP} and W_{LPP} are the weight fraction of the IPP and LPP components, respectively. Heat of fusion for PP with 100 % crystallinity, ΔH^* , was assumed to be 209 J/g [19].

$$X_{c-IPP}(\%) = \frac{\Delta H_{IPP}}{\Delta H^*} \times \frac{1}{W_{IPP}} \times 100 \quad (3)$$

$$X_{c-LPP}(\%) = \frac{\Delta H_{LPP}}{\Delta H^*} \times \frac{1}{W_{LPP}} \times 100 \quad (4)$$

3. Results and Discussion

3.1 Melt spinning behavior and observation of fiber cross-section

The contraction ratio after the spinning was plotted against the total IPP content in Fig.1. The sheath layer

Fig. 1 Variation of the contraction of as-spun IPP/LPP bicomponent fibers after spinning with total IPP content and sheath layer composition.

Fig. 2 Cross-section of various as-spun IPP/LPP bicomponent fibers with different sheath layer composition observed with TEM.

composition is also indicated in the figure. The contraction ratio decreased continuously from 15 to 7 % with the increase of IPP content from 0 to 5 %.

Cross-sections of the as-spun fibers containing carbon black in the sheath layer were observed under a TEM as shown in Fig.2. Boundary between the sheath and core components was clearly observed. It was confirmed from these results that the cross-sectional configuration of the bicomponent fibers of various sheath/core compositions were controlled with high accuracy in the spinning process.

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 total IPP content of 0 and 5 wt% are compared in Fig.3. There was a significant change in the stress-strain behavior between the first and the second stretchings. It should be noted that almost identical behaviors were observed between the second and the third stretchings. A certain level of hysteresis was observed between the stretching and recovery even after the second stretching. By adding

Fig. 3 Stress-strain hysteresis curves for the first, second and third cycles of stretching and recovery of as-spun IPP/LPP fibers with the total IPP content of 0 and 5 wt%.

5 wt% of IPP, there was a significant increase in the tensile stress. In addition, a slight yielding behavior was observed during the first stretching. Elastic recoverability also decreased by adding 5 wt% of IPP.

It should be noted that the strain at which the stress became zero during the recovery was slightly higher than that during the second stretching especially for the IPP/LPP fiber. It means that there was an additional contraction of fiber sample with time after returning the cross-head of the tensile testing machine to the original position for recovery. This phenomenon was considered to be due to the viscoelastic effect.

Fig. 4 Variation of elastic recovery of as-spun IPP/LPP bicomponent fibers with total IPP content and sheath layer composition.

Variation of elastic recovery after the first stretching with the increase of total IPP content is shown in Fig.4. All samples showed relatively large elastic recovery of higher than 85%, while the elastic recovery slightly decreased with the increase of total IPP content.

Tensile modulus of as-spun fibers is plotted against the total IPP content in Fig. 5. Tensile modulus increased with the total IPP content and also with the increase in the thickness of sheath layer. This result corresponds to the reduction of contraction after spinning with the increase of the total IPP content, since the higher tensile modulus

leads to the lower degree of elastic stretching in the spinline. In addition, increase of tensile modulus of 2.5 times, i.e. from 40 MPa for pure LPP fiber to around 100 MPa for LPP/IPP bicomponent fibers with overall IPP content of 5wt% corresponded to the reduction of elastic contraction of 56% (from 16% to 7%). It should be noted that $(100/40) \times (7/16)$ is close to unity, indicating that the variations of tensile modulus and contraction after spinning matched quantitatively.

Increase in the tensile modulus of as-spun fibers with the increase of total IPP content indicated that the

Fig. 5 Variation of tensile modulus of as-spun IPP/LPP bicomponent fibers with total IPP content and sheath layer composition.

Fig. 7 Variation of tensile strength of as-spun IPP/LPP bicomponent fibers with total IPP content and sheath layer composition.

Fig. 6 Variation of the estimated tensile modulus of the sheath component of as-spun IPP/LPP bicomponent fibers with total IPP content and sheath layer composition.

Fig. 8 Variation of strain at break of as-spun IPP/LPP bicomponent fibers with total IPP content and sheath layer composition.

blending of 10 wt% of IPP caused the increase in the tensile modulus of the sheath component. Assuming the constant tensile modulus of 38 MPa for the core component, which corresponds to the value for the as-spun fiber with the total IPP content of 0 wt%, tensile modulus of the sheath component was estimated based on a simple parallel model. The obtained tensile modulus increased from 174 to 283 MPa with the decrease of the total IPP content as shown in Fig.6. This result suggested that the smaller amount of sheath component yielded its higher tensile modulus even though the IPP content in the sheath was constant.

Tensile strength and elongation at break of the as-spun fibers are plotted against the total IPP content in Figs. 7 and 8, respectively. The tensile strength increased whereas the elongation at break was almost constant with the increase of the total IPP content.

In comparison with the elongation at break of unoriented LPP films (900%) [15], the prepared fibers showed relatively low elongation at break of about 200 %. This is presumably because of the development of molecular orientation under the spinning condition for the production of spun-bonded non-woven fabrics. To confirm this consideration, structural analysis of as-spun fibers were conducted.

3.3 Fiber structure

Structure analysis of as-spun fibers was performed and compared with the mechanical properties. WAXD patterns of the as-spun fibers of various sheath/core compositions are shown in Fig.9. All as-spun fibers

exhibited similar WAXD patterns with highly oriented α -form crystals. Effect of neither sheath/core composition nor IPP content on the characteristics of WAXD pattern was observed.

We have reported that in 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 crystal of virtually no orientation [20]. This was because the crystallization of IPP occurred in the spin-line at a relatively high temperature before the crystallization of LPP. This caused the stopping of the thinning of spin-line. Accordingly, orientation relaxation of LPP component proceeded. If crystallization of the LPP occurred in the spin-line at a temperature much lower than the crystallization temperature of IPP or even after the winding up of as-spun fibers on the bobbin, α -form crystals of no-orientation could be formed.

Based on the consideration stated above, it can be speculated that even though crystallization of IPP component started to occur at higher temperatures, deformability of the sheath component was maintained because the content of IPP was only 10 wt% in the LPP/IPP blend. Accordingly orientation of the core component, LPP, could proceed in the spin-line and highly orient α -form crystal was formed.

Variation of overall birefringence of as-spun fibers with the total IPP content and sheath layer composition is shown in Fig.10. The overall birefringence increased with the increase of the thickness of sheath component. It can

Fig. 9 Wide-angle X-ray diffraction patterns of as-spun IPP/LPP bicomponent fibers of six different sheath layer compositions.

be speculated that the sheath component, IPP/LPP blend, has higher crystallizability than LPP, and the enhanced crystallization of the sheath component could result in the stress concentration and the enhanced development of orientation in the sheath component. In addition, it can be speculated that the crystallinity increases with the increase of IPP content in LPP/IPP blend. As shown in Fig.9, crystals are highly oriented along the fiber axis. Larger amount of highly oriented crystals can be the reason for the increase of birefringence, i.e. total molecular orientation, with the increase of the total IPP content.

Since birefringence measurement was performed at the center of the fibers, measured birefringence of the as-spun fibers can be expressed using the birefringences of sheath and core components, Δn_{sheath} and Δn_{core} , as described in equation (5), where W_{core} is the weight ratio of the core component. Using the equation (5), birefringence of the sheath component was estimated assuming the constant birefringence of the core component to be 9.9×10^{-3} , which corresponds to the birefringence of the as-spun LPP fiber with the IPP content of 0 wt%.

$$\Delta n_{Ave} = \sqrt{W_{core}} \Delta n_{core} + (1 - \sqrt{W_{core}}) \Delta n_{sheath} \quad (5)$$

Estimated birefringence of the sheath component is plotted against total IPP content and sheath layer composition in Fig.11. Except for the total IPP content of

1 wt%, birefringence of the sheath component was almost constant at around 15×10^{-3} , which was profoundly higher than the birefringence of the core component. This result supported our previous discussion on the increase of birefringence caused by the increase of crystallinity by the blending of IPP.

DSC curves of as-spun fibers are shown in Fig.12. Melting peaks of the LPP and IPP components were detected at 50 - 80 °C and around 165 °C, respectively. The melting peak of LPP was consisting of two peaks, a relatively sharp peak at lower temperature of around 50 °C and a relatively broad peak at higher temperature of around 75 °C. The height of the lower temperature peak tended to decrease in comparison with the peak area of the higher temperature peak of 75 °C with increasing total IPP content. On the other hand, the area of the melting peak of IPP at around 165 °C increased with the increase of IPP content as expected.

Melting enthalpies for IPP and LPP components were analyzed from the DSC thermograms. Figure 13 shows the variations of the melting enthalpies of IPP and LPP as well as the total melting enthalpy with the changes of the total IPP content and the sheath-layer ratio. If crystallinity of the pure IPP and LPP, X_{c-IPP} and X_{c-LPP} , do not change with the total IPP content, the enthalpy of melting for IPP, LPP and total are expected to increase, decrease by 5% and increase linearly, respectively, with the increase of total IPP content from 0 to 5 wt%. In these cases, enthalpy changes corresponding to the variation of

Fig. 10 Variation of overall birefringence of as-spun IPP/LPP bicomponent fibers with total IPP content and sheath layer composition measured under polarizing microscope at the center of individual fiber.

Fig. 11 Variation of birefringence of sheath layer of as-spun IPP/LPP bicomponent fibers with total IPP content and sheath layer composition. Birefringence of the sheath layer was estimated assuming the constant birefringence in the core.

Fig. 12 DSC thermograms of as-spun IPP/LPP bicomponent fibers of six different total IPP contents.

total IPP content from 0 to 5 wt% are supposed to be from 0 to $\Delta H^* \times X_{c-IPP} \times 0.05$ for IPP, from $\Delta H^* \times X_{c-LPP}$ to $\Delta H^* \times X_{c-LPP} \times 0.95$ for LPP, and from $\Delta H^* \times X_{c-LPP}$ to $\Delta H^* \times (X_{c-IPP} \times 0.05 + X_{c-LPP} \times 0.95)$ for the total. In other words, total melting enthalpy was expected to increase with the increase of total IPP content. Instead of this, experimental result showed the significant reduction of total melting enthalpy with the increase of IPP content. This was because the melting enthalpy for IPP increased and showed a slight tendency of saturation while the melting enthalpy for LPP decreased significantly with the increase in the IPP content.

Fig. 13 Variations of heat of fusion of LPP, IPP and total components of as-spun IPP/LPP bicomponent fibers with total IPP content and sheath layer composition.

From the DSC thermograms, crystallinity of LPP and IPP components were analyzed and plotted against the total IPP content as shown in Figs.14 and 15. Crystallinity of LPP component decreased from 15 to 12 % with the increase of total IPP content from 0 to 5 wt%. On the other hand, crystallinity of the IPP component decreased from about 60 to 40%. It should be noted that the crystallinity of the fibers of IPP used in this research is around 40-50%. In other words, in the melt spinning of bicomponent fibers, there was a mutual interaction between the sheath and core components in that the crystallization of the IPP component was enhanced especially when the sheath layer composition was low while that of the LPP was significantly suppressed. For more detailed discussion in terms of structure development behavior, crystallinity of LPP in sheath and core components needs to be evaluated separately.

3.4 Mechanism of structure formation in sheath-core fibers

Gathering the experimental results stated above, mechanism of fiber structure development in the bicomponent melt spinning of LPP and LPP/IPP blend can be speculated as follows. Firstly, if spinning behavior of the LPP and IPP single component spinings of the same extrusion condition are compared, IPP should show much steeper thinning behavior with the solidification position closer to the spinneret because of its higher crystallizability. Thinning behavior of the LPP/IPP blend with the IPP content of 10 wt% should be somewhere in between those for pure LPP and pure IPP. In this case,

Fig. 14 Variation of crystallinity of LPP component in as-spun IPP/LPP bicomponent fibers with total IPP content and sheath layer composition.

Fig. 15 Variation of crystallinity of IPP component in as-spun IPP/LPP bicomponent fibers with total IPP content and sheath layer composition.

according to the results of our previous research [21,22], molecular orientation and crystallization of LPP component in the bicomponent fiber should be suppressed in comparison with its single component spinning. Oppositely, those of LPP/IPP blend component should be enhanced. However, effect of such mutual interaction on the core component (LPP) should be minimal if IPP content of only 10 wt% in the sheath is considered. This is the reason why WAXD patterns shown in Fig.9 exhibited crystalline reflections of highly oriented α -form crystals indicating that fairly high degree of molecular orientation was maintained in the core component. On the other hand, it should be noted that in the bicomponent spinning, changes of structure and properties of the component with lower composition and lower viscosity is expected to be affected more significantly in comparison with its single component spinning. These considerations matched with the experimental results shown in Figs. 6 and 11, that is, tensile modulus and birefringence of the sheath component, which were estimated based on the assumption that the structure and properties of the core component are constant, were higher than those for the core component because of the incorporation of IPP with higher crystallizability, and more importantly those values increased with the decrease of the sheath layer composition.

4. Conclusions

Sheath-core type bicomponent fibers melt-spun

using the LPP/IPP blend with IPP content of 10 wt% as the sheath component and pure LPP as the core component showed elastomeric property with reasonably good elastic recovery of higher than 85 wt%, while the elastic recovery slightly decreased with the increase of sheath layer composition from 0 to 50 wt%, which corresponds to the increase of total IPP content from 0 to 5 wt%. Tensile modulus and tensile strength of the as-spun bicomponent fibers increased significantly with the increase of total IPP content. Through the structural analyses of as-spun fibers consisting of LPP and IPP, it was found that the crystallization of IPP component was enhanced especially when the composition of sheath component was low while that of LPP was suppressed significantly with the increase of the total IPP content. These results suggested the high modulus of sheath component for the fibers with low sheath layer composition.

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