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ORIGINAL ARTICLE

Structure and mechanical anisotropy of injection-molded polypropylene with a plywood structure

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Injection-molded isotactic polypropylene (PP) containing a small amount of the β-nucleating agent *N*,*N*′-dicyclohexyl-2,6-naphthalenedicarboxamide exhibits a unique molecular orientation that is similar to that of plywood. X-ray diffraction and birefringence distribution measurements revealed that PP chains in β-form crystals are oriented perpendicular to the flow direction through epitaxial crystallization on the needle-shaped nucleating agent, even in the skin layer. Furthermore, PP chains in α-form crystals orient along the flow direction through flow-induced crystallization. Although the skin has a 'woven-cloth' structure in which the two crystalline forms are oriented perpendicular to each other, it shows positive birefringence, on average, because of the stronger orientation of α-form crystals. In the core, not only β-form crystals but also α-form crystals are oriented perpendicular to the flow direction. As the average orientation direction in the skin layer is perpendicular to that in the core, the dynamic tensile modulus in the flow direction is almost identical to that in the transversal direction, resulting in a low level of mechanical anisotropy. Moreover, the anisotropy in thermal expansion is greatly reduced by the extraordinary molecular orientation.

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Keywords: injection-molding; mechanical anisotropy; polypropylene

INTRODUCTION

Injection molding is one of the most widely available processing methods for isotactic polypropylene (PP). The resultant products are characterized by the well-known 'skin-core structure'. As a result of the high level of molecular orientation obtained with rapid cooling, accelerated crystallization, known as flow- or shear-induced crystallization, occurs in the skin layer.[1–15] The crystalline structure in the skin layer is a shish-kebab structure, which is markedly different from the spherulite texture of the core layer.[14–20] The marked molecular orientation provides a high modulus in the flow direction; however, anisotropy in thermal and mechanical properties, which is an inherent characteristic of injection-molded products, causes severe problems in industrial applications, including shrinkage, warping and dimensional instability.[21–26] Moreover, it has been recently reported that an injection-molded plate of PP containing the β-nucleating agent *N*,*N*′-dicyclohexyl-2,6-naphthalenedicarboxamide exhibits a unique molecular orientation that is similar to that of plywood.[27]

In our previous studies,[27–32] it was revealed that *N*,*N*′-dicyclohexyl-2,6-naphthalenedicarboxamide is dissolved in molten PP above 260 °C and appears as needle-shaped crystals at 240 °C during the cooling procedure. From the surface of the needle-shaped crystals, PP molecules epitaxially crystallize in the β trigonal crystalline form, in which the *c*-axis (chain-axis) of PP orients perpendicular to the long axis of the needle-shaped crystals. Under an applied flow field in extrusion processing, the needles orient along the flow direction before PP crystallization because of the hydrodynamic force. As a result, the *c*-axis of PP orients perpendicular to the applied flow direction. In the case of an injection-molding product, PP chains show positive birefringence, meaning they orient along the flow direction, in the skin layer, presumably due to flow-induced crystallization, even for the product containing the nucleating agent. On the contrary, the orientation direction of PP chains in the core layer is found to be perpendicular to the flow direction because of crystal growth from the nucleating agent when the mold temperature is controlled at 80 °C or higher. Owing to this unique morphology, mechanical toughness is greatly improved. However, the detailed structure and mechanical properties of the samples have not been clarified yet.[27] Moreover, the structure and properties have not been compared with those of a pure PP product prepared at conventional mold temperatures, which has the thermodynamically stable α monoclinic crystalline form.

Therefore, in this study, the molecular orientation and crystalline structural details, including the degree of crystallinity and the crystalline form, are characterized in detail by X-ray diffraction and other methods and are compared with those of an injection-molded product lacking the nucleating agent that is obtained at conventional cooling conditions. Furthermore, the anisotropy of dynamic mechanical and tensile properties and of thermal expansion behavior of an

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injection-molded plate with a plywood structure is investigated in detail. The anomalous molecular orientation of PP is expected to reduce the anisotropy of these properties.

EXPERIMENTAL PROCEDURE

Materials and sample preparation

Commercially available isotactic PP (Sumitomo Chemical, Tokyo, Japan; FLX80E4, MFR = 10 (g per 10 min), $M_n = 68\,000$ and $M_w = 209\,000$) was used. The stereoregularity is 96% (*mmmm*%, a meso-pentad value), and it contains no comonomer.

PP containing 0.05 wt% of *N*,*N*′-dicyclohexyl-2,6-naphthalenedicarboxamide (New Japan Chemical, Osaka, Japan; NJ Star^{TR} NU-100) was extruded by a co-rotating twin-screw extruder (Technovel, Osaka, Japan; KZW15TW-45MG-NH) at 260 °C with a thermal stabilizer. The screw rotation speed was 250 r.p.m., and the output rate was approximately 4.0 kg h^{-1}. The diameter of the screw was 15 mm, and the length-to-diameter ratio was 45. Before melt mixing, all powder materials were mixed at room temperature and fed into the hopper feeder. The extruded strands were immediately quenched in a water bath and subsequently cut by a strand cutter. Moreover, PP without the nucleating agent was prepared following the same method as a reference sample.

Injection-molded plates (35 mm in width and 40 mm in length) with a thickness of 1.0 mm were prepared using an injection-molding machine (Nissei Plastic Corporation, Tokyo, Japan; PS40E5ASE). The temperature of the mold with a film-gate was controlled at 120 °C. Injection molding was conducted at the following conditions: temperature profile of the barrel (C1/180 °C, C2/190 °C, C3/195 °C and C4/200 °C); injection pressure, 11.7 MPa, holding pressure, 1.4 MPa; cooling time, 30 s; and screw rotation speed, 100 r.p.m. The 1.0-mm-thick reference plate without the nucleating agent was prepared at 40 °C, which is a conventional mold temperature for PP.

Measurements

The density of the injection-molded plates was measured with a top-loading electronic balance using a floatation method. As the tests were conducted at a constant temperature (23 °C), the density of water was assumed to be 997.5 kg m^{-3}.

Thermal analysis was conducted with a differential scanning calorimeter (Mettler-Toledo International, Greifensee, Switzerland, DSC820) under a nitrogen atmosphere to avoid thermal-oxidative degradation. Samples of approximately 10 mg in weight were sealed in aluminum pans. Melting profiles were recorded at a heating rate of 10 °C min^{-1}.

The distribution of the orientation birefringence in the thickness direction was measured by a polarized microscope (Leica Microsystems, Wetzlar, Germany, DMLP) with a tilting compensator. Film specimens with 10 μm thickness were excised using an ultra-microtome (Leica, FCS) at −60 °C parallel to the flow direction in the MD (machine direction)—ND (neutral and thus thickness direction) plane.

Wide-angle X-ray diffraction (WAXD) patterns were measured by using a graphite-monochromatized Cu Kα radiation beam focused via a 0.3-mm pinhole collimator with a flat 20 × 20 cm^2 imaging plate detector of 1900 × 1900 pixels (Rigaku, Akishima, Japan, R-AXIS IIc). A small piece of the sample with edges of <1 mm was mounted with a sample-imaging plate distance of 10 cm. The exposure was performed with shots of 7 min in duration by directing the X-ray beam along the normal direction of the plate, the through view.[28] In this study, the entire plate with 1.0 mm thickness was initially measured. Further, certain specimens were used to evaluate the molecular orientation in the skin and core layers. For the skin layer, one side of the plate was ground in water until a sample with a thickness of 0.3 mm remained. In the case of the core layer, each side was reduced by 0.25 mm. The thickness of the reduced area was determined by considering the birefringence distribution results.

The temperature dependence of the dynamic tensile moduli was measured from −100 to 165 °C using a dynamic mechanical analyzer (UBM, Mukou, Japan, DVE V-4). The frequency was 10 Hz, and the heating rate was 2 °C min^{-1}. Rectangular specimens, 3 mm wide and 15 mm long, were cut out from the plates. To examine mechanical anisotropy, two types of samples were prepared: one was parallel to the flow direction (MD sample), and the other was perpendicular to the flow direction (TD sample). Therefore, in the case of the MD sample, the direction of the oscillatory strain applied coincides with the flow direction.

Stress-strain curves were measured at room temperature using a tensile machine (Tokyo Testing Machine, Toyohashi, Japan, SBR-500N) following ASTM D638. The sample specimens were cut out from the plate by a razor blade. The shape of the specimen followed JIS K6301 Dumbbell #3, although the sample size was reduced by 40%. The initial distance between the gauges was 20 mm, and one gauge moved at a constant speed of 100 mm min^{-1}. All measurements were performed at least five times, and the average values were calculated. The elongation at the break point was evaluated by measuring the final gauge length of the narrow part of the dumbbell.

The linear coefficient of thermal expansion was measured using a thermo-mechanical analyzer (Bruker, Billerica, MA, USA, TAPS3000S) in compression mode under a constant stress of 3.2 kPa and at a heating rate of 2 °C min^{-1}. The temperature was controlled from −20 to 100 °C. The initial length of the specimen was 2.5 mm, and the cross-sectional area was approximately 2.7 mm^2. The linear coefficient of thermal expansion β was defined by the following equation:

$$\beta = \frac{1}{L_0}\frac{dL}{dT} \qquad (1)$$

where L_0 is the initial length of the specimen.

RESULTS AND DISCUSSION

Characterization of injection-molded PP

As discussed in our previous paper,[27] injection-molded plates containing the nucleating agent have a unique molecular orientation, which is similar to that of plywood when the mold temperature is maintained between 80 and 120 °C. In this structure, PP molecules orient along the flow direction in the skin layer but along the TD (transversal direction) and ND in the core layer. Although a preliminary characterization was performed in the previous study,[27] the degree of crystallinity and the molecular orientation of each crystalline form in the skin and core layers have not been revealed. As they are important to mechanical properties, detailed characterizations of the injection-molded plate were conducted in this study.

The melting behavior of the plate is shown in Figure 1. As shown in the figure, pure PP has a distinct melting peak at 167.1 °C, ascribed to α-form crystals. On the contrary, PP containing the nucleating agent

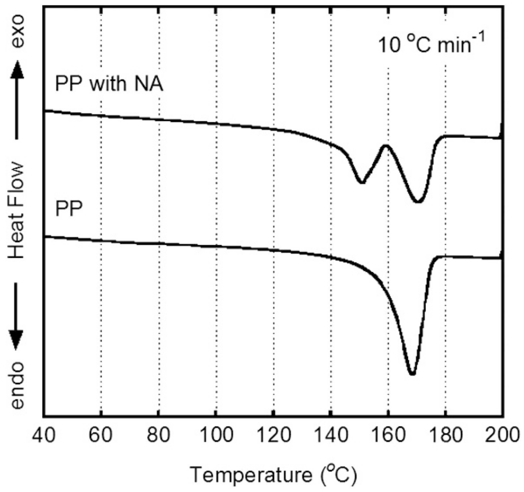

Figure 1 Differential scanning calorimetry heating curves of injection-molded plates at a heating rate of 10 °C min^{-1}.

Table 1 Characteristics of injection-molded product

	Melting temperature (°C)		*Heat of fusion (J/g)*		*Degree of crystallinity (%)*		*Density*
	β-Form	*α-Form*	*β-Form*	*α-Form*	*β-Form*	*α-Form*	*(kg m^{-3})*
PP	—	167.1	—	95.4	—	56	905
PP with NA	149.6	169.8	41.6	60.6	25	36	902

Abbreviations: NA, Nucleating agent; PP, polypropylene.

has intense double peaks at 149.6 and 169.8 °C because of melting β- and α-form crystals, respectively. However, the differential scanning calorimetry profile does not correspond with the crystalline form in the plate because the recrystallization of α-form crystals occurs immediately after the β-form crystals melt during the differential scanning calorimetry measurement. In other words, the melting peak ascribed to α-form crystals is composed of two contributions: one from α-form crystals in the original plate and another from the recrystallized ones after melting of β-form crystals.

Table 1 summarizes the heats of fusion for α- and β-form crystals, along with density data for the plates measured by the flotation method at room temperature. Assuming that the heats of fusion of perfect crystals of α- and β-form PP are 170 and 168.5 J g^{-1},[33] the degree of crystallinity for pure PP is calculated as 56% (95.4 J g^{-1}). However, the total heat of fusion of PP containing the nucleating agent is 102.2 J g^{-1}, with 41.6 J g^{-1} contributed by the β-form (25% crystallinity) and 60.6 J g^{-1} contributed by the α-form (36% crystallinity). The heat of fusion of α-form crystals, however, does not provide information for the solid state of the plate because recrystallization occurs during the differential scanning calorimetry measurement after β-form crystals melt.

Furthermore, the density of PP containing the nucleating agent is almost identical to that of pure PP, although the density of β-form crystal (921 kg m^{-3}) is lower than that of α-form crystal (936 kg m^{-3}).[34] These results suggest that the plate containing the nucleating agent has a high degree of crystallinity.

Figure 2 shows the birefringence distribution along the thickness direction of the thin films sliced parallel to the MD-ND plane and cut from the plates. For pure PP, the orientation birefringence has positive values, demonstrating that PP chains orient along the flow direction in the skin layer. On the contrary, an undeformed spherulite texture is detected in the core layer, demonstrating that birefringence is zero on average.

In PP containing the nucleating agent, the birefringence has negative values in the core layer lacking the spherulite texture. These results indicate that PP crystals grow from the surface of the nucleating agent epitaxially. For the skin layer, however, flow-induced crystallization seems to determine the average direction of molecular orientation.

Figure 3 shows WAXD patterns of the entire plate, in which the diffraction curves are transformed and corrected for Lorentz and polarization (Lp) factors. The X-ray beam was inserted in the normal direction: that is, in the through view. The peaks were separated over the amorphous background scattering (Bg), which was approximated by a smooth spline curve.

As shown in Figure 3a, the α-form crystal is predominantly detected in the pure PP plate, in which the intensity ratio is nearly α:β:Bg≈38:0:62. However, the β-form crystal, indicated by arrows in Figure 3b, appears predominantly in PP containing the nucleating agent, with sporadic occurrences of the α-form crystal. The intensity ratio is nearly α:β:Bg≈16:32:52. The crystallinity result qualitatively corresponds to the density and thermal measurements.

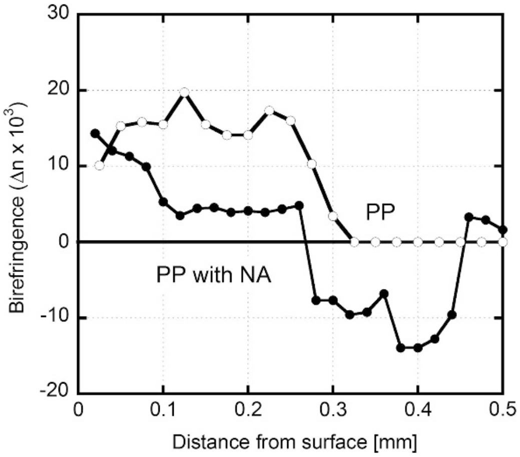

Figure 2 Distribution of orientation birefringence for thin slices (parallel to machine direction (MD)– neutral direction (ND) plane) of pure polypropylene (PP; open symbol) and PP containing the nucleating agent (closed symbol). The identical data for PP containing the nucleating agent were reported previously.[27]

The orientation direction of the α- and β-form crystals is not clearly detected in the pictures because of overlapping of the scattering profiles from the skin and core layers. Therefore, molecular orientation is further discussed using data from the skin and core layers.

Figure 4 shows WAXD patterns of the skin and core layers of the injection-molded plates. Figures 4a and c are diffraction patterns passing through the skin layer (0.3 mm thickness), whereas Figures 4b and d are patterns passing through the core layer (0.5 mm thickness) of the plate. As shown in Figure 4a, distinct arcs are detected for pure PP and are ascribed to (110), (040), (130) and (111) reflections of the α-form crystals from a low angle. This result shows that α-form crystals strongly orient along the MD, indicating a highly oriented structure along the flow direction, presumably with a shish-kebab structure. The TD orientation of the (110) reflection in the α-form crystals is explained by the daughter lamellae,[35] which grow approximately perpendicular to the mother lamellae oriented along the flow direction. For the core layer, four diffraction rings attributed to α-form crystals are clearly observed in Figure 4b, suggesting weak or no orientation. This result is reasonable because molecules relax the orientation in the core layer and crystallize into an undeformed spherulite texture.

For PP containing the nucleating agent, Figure 4c clearly shows that the plate is composed of both α- and β-form crystals, with an intensity ratio of α:β:Bg≈20:19:61 in the skin layer. Although the α-form crystal appears because of intense shear flow, which orients along the flow direction, almost the same amount of the β-form crystal is also observed distinctly. Moreover, it should be noted that the orientation direction for the β-form crystals is perpendicular to the flow direction. As a result, the orientation of PP chains is reduced on average. This result can explain the low positive values of the orientation birefringence in Figure 2. The molecular orientation in the skin layer, parallel to the flow direction for α-form crystals and perpendicular for the β-form, is similar to the structure of a woven cloth, in which α- and β-form crystals act as the warp and woof, respectively.

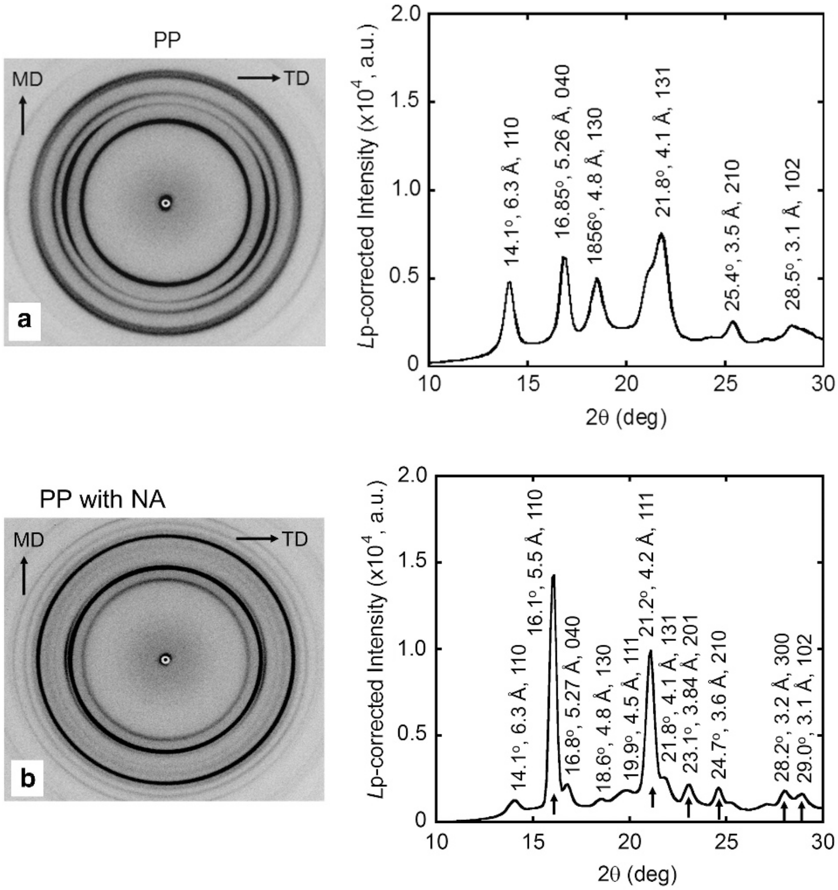

Figure 3 Wide-angle X-ray diffraction (WAXD) patterns with the Lp-corrected curve of an entire plate of (**a**) pure polypropylene (PP) and (**b**) PP containing the nucleating agent. The 2θ angle, *d* spacing, and *hkl* indices are assigned in the figure, and the peaks attributed to β-form crystals are indicated by arrows in (**b**).

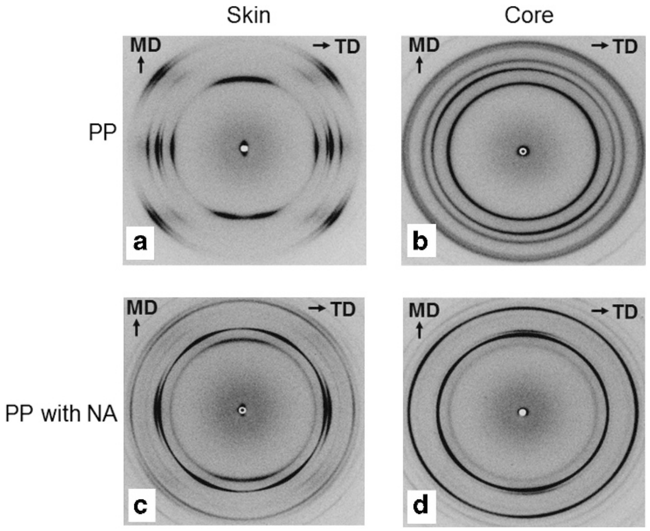

Figure 4 Wide-angle X-ray diffraction (WAXD) patterns of injection-molded plates: (**a**) the skin layer for pure polypropylene (PP), (**b**) the core layer for pure PP, (**c**) the skin layer for PP containing the nucleating agent and (**d**) the core layer for PP containing the nucleating agent.

As shown in Figure 4d, strong diffraction of the β-form crystals corresponding to (110) and (111) reflections is detected with the weak intensity of the α-form crystals in the core layer, demonstrating that β-form crystals are observed distinctly in the core layer because of an appropriate crystallization temperature (100–140 °C) that promotes β-form crystallization. Moreover, the strong intensity in the poles for the (040) reflection of the α-form crystals indicates TD orientation in the core layer, in accordance with the (110) plane of the β-form crystal. The result can be explained by previous work on the β–α growth transition induced in this specific temperature range.[36] As a result, both α- and β-form crystals have TD orientation in the core.

To better understand the orientation direction of PP crystals in the plate containing the nucleating agent, an azimuthal intensity distribution scan was performed using the data in Figures 4c and d, in which the features of the diffraction patterns suggest preferred orientations of the α- and β-form crystals. In their respective narrow 2θ ranges, the pixel intensities were collected and plotted against the azimuthal angle φ defined on the imaging plate detector. The angle φ is associated with the azimuthal angle φ_M pointing along lattice direction (*hkl*), which is defined to be normal to the corresponding (*hkl*) crystal face.

As shown in Figure 5a, the intensity maxima of the (110) reflection in the β-form crystals in the skin layer appear at $\varphi_M \approx 30$, 90 and 150°. This result shows that the *c*-axis in the β-form crystals orients preferentially along the transversal direction, and the growth direction is along the horizontal (110), even in the skin layer. However, the (110) reflection in the α-form crystals has a broad peak at $\varphi_M \approx 0°$, indicating that the α-form crystals preferentially orient along the MD. Moreover, the azimuthal data display similar behavior for the β-form

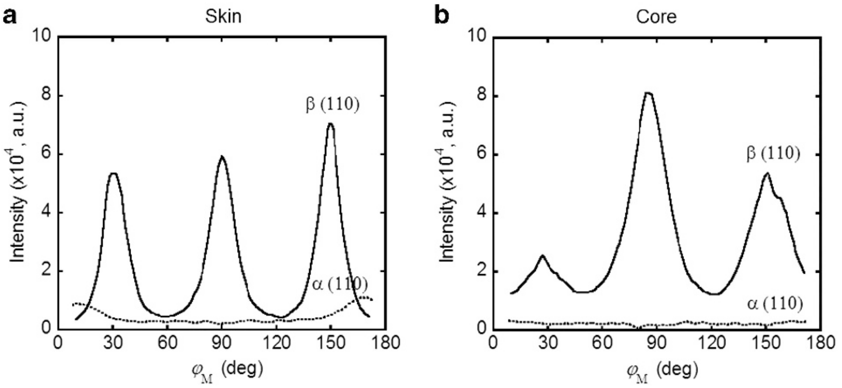

Figure 5 Azimuthal intensity distributions of the (110) reflection of the α-form crystal (dotted line) and the (110) reflection of the β-form crystal (solid line) vs φ_M of the plate containing the nucleating agent: (**a**) skin and (**b**) core layers.

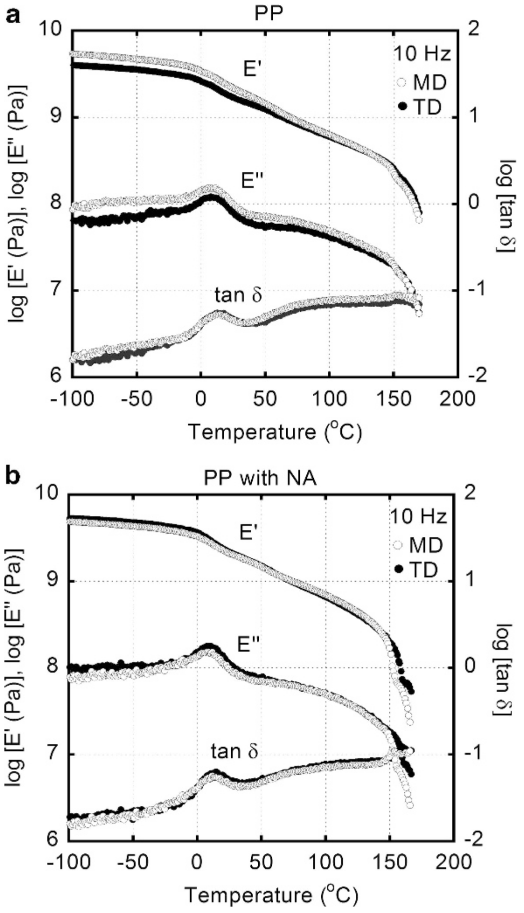

Figure 6 Temperature dependence of tensile storage modulus *E*′, tensile loss modulus *E*″, and loss tangent *tan δ* in machine direction (MD; open symbols) and transversal direction (TD; closed symbols) directions for the injection-molded plate at 10 Hz of (**a**) pure polypropylene (PP) and (**b**) PP containing the nucleating agent.

crystal in the core layer (Figure 5b). However, the intensity distribution of the (110) reflection in the α-form crystal is very low and uniform, demonstrating that a small number of α-form crystals grow in the core layer without orientation. Although there is no orientation for the (110) reflection, the equatorial spots of (040) indicate the parallel orientation to (110) of the β-form crystal mentioned above. Finally, it should be noted again that MD orientation of the β-form crystals is not detected in the skin or core layers.

On the basis of the birefringence distribution and WAXD profiles, the molecular orientation in the injection-molded plate of PP containing the nucleating agent is thus determined: PP chains in α-form crystals preferentially orient along the flow direction in the skin layer because of flow-induced crystallization. In contrast, β-form crystals exhibit perpendicular orientation to the flow direction, even in the skin layer, leading to a low level of average molecular orientation along the flow direction with a ‘woven cloth’ structure. β-Form crystals are predominantly detected in the core layer, in which PP chains orient perpendicular to the flow direction. α-Form crystals in the core also show perpendicular orientation with the β-form crystals, although the core layer contains a small number of α-form crystals.

Mechanical properties

Figure 6 shows the temperature dependence of the dynamic tensile modulus. As evident in Figure 6a, both moduli in the MD sample are higher than those in the TD sample at low temperatures for pure PP. However, both moduli show almost the same values (especially *E*′) at high temperature (beyond α dispersion). This result is reasonable because the mechanical properties for injection-molded products are affected by the molecular orientation in the skin layer, in which PP molecules orient along the flow direction on average. This phenomenon has been well documented by numerous studies of injection-molded PP.[5,10,37–42]

In contrast, as shown in Figure 6b, tensile moduli in the MD sample are similar to those in the TD sample over a wide temperature range for PP containing the nucleating agent. In the present sample, with unique molecular orientation similar to that of plywood, PP chains in α-form crystals preferentially orient along the flow direction in the skin layer, especially at the surface. On the contrary, perpendicular orientation to the flow direction is predominant in β-form crystals, which is most noticeable in the core layer. As a result, the molecular orientation of PP chains in the skin and core layers is canceled out on average. This result is reasonable because the thickness and absolute value of birefringence are almost similar for the skin and core layers. This result also shows that the mechanical anisotropy of the sample is greatly reduced.

Moreover, PP containing the nucleating agent exhibits high storage moduli despite the large number of β-form crystals. This result will be

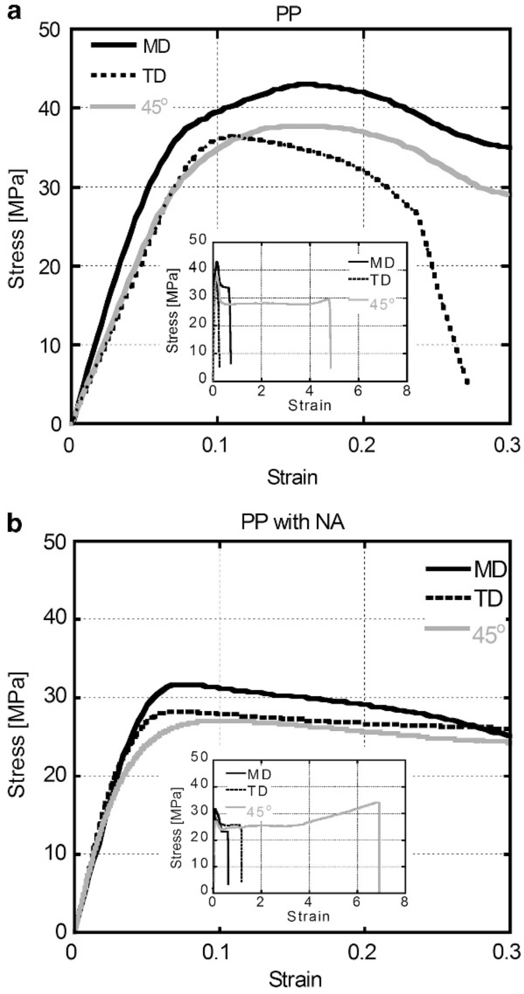

Figure 7 Engineering stress-strain curves at various stretching directions of the injection-molded plates at room temperature: (**a**) pure polypropylene (PP) and (**b**) PP containing the nucleating agent. The strain rate is $0.083\,s^{-1}$.

Table 2 Tensile properties

Sample	*Stretching direction*	*Young's modulus (MPa)*	*Yield stress (MPa)*	*Strain at yield point*	*Stress at break (MPa)*	*Strain at break*
Pure PP	MD	590	42.8	0.150	33.1	0.65
	45°	440	37.7	0.145	29.2	4.80
	TD	430	36.4	0.110	26.6	0.24
PP with NA	MD	655	31.6	0.080	20.5	0.62
	45°	650	27.0	0.090	34.1	6.75
	TD	740	28.2	0.075	22.9	1.20

Abbreviations: MD, machine direction; NA, Nucleating agent; PP, polypropylene; TD, transversal direction.

discussed below with tensile test results. The peak temperature of loss modulus E'', ascribed to T_g, is not affected by the direction of oscillatory strain and the presence of the nucleating agent.

The stress-strain curves at room temperature are shown in Figure 7. The strain rate is $0.083\,s^{-1}$. The tensile force is applied along the direction of MD (0°), 45° and TD (90°). The results are summarized in Table 2.

As seen in Figure 7 and Table 2, the marked difference in the tensile behavior between MD and TD stretching is detected for pure PP. Young's modulus and the yield stress in MD stretching are considerably higher than those in TD stretching. These differences are attributed to the molecular orientation in the skin layer, as observed in conventional injection-molded plates.

For PP containing the nucleating agent, the anisotropy in Young's modulus is weaker than that for pure PP, which corresponds with the dynamic tensile moduli in Figure 6. As this plate has extraordinary molecular orientation, the anisotropy of the modulus is reduced. Further, it should be noted that Young's modulus in MD stretching of PP containing the nucleating agent (655 MPa) is higher that of pure PP (590 MPa), although PP chains orient perpendicular to the flow direction in the core layer. Moreover, TD orientation in the core layer provides higher Young's modulus when TD stretching to a great extent. Young's modulus in TD, 740 MPa, is considerably higher than that of pure PP (430 MPa). The modulus of PP containing a large number of β-form crystals is believed to be lower than that with α-form crystals because of the loose packing of PP chains in the β-form crystal.[43–46] However, this study demonstrates that PP products containing a large number of β-form crystals can have high moduli. This result is explained by the enhanced crystallinity for the sample, as revealed by density, differential scanning calorimetry and WAXD measurements, suggesting the strong nucleating ability of the nucleating agent used.

In the case of yield stress, MD stretching gives a higher value than TD stretching, although most molecular chains orient perpendicular to the flow direction in the core layer. This result is attributed to a large number of tie molecule fractions along the flow direction. The flow field applied in the molten state during processing leads to anisotropy in the tie molecule fraction, as explained in detail in our previous paper.[30] Moreover, numerous microvoids are generated during MD stretching.[32] On the contrary, in TD stretching, shear yielding is dominant, indicating that reorganization and phase transformation of crystalline structure occur easily with low yield stress. Compared with pure PP, lower yield stress is detected for PP containing the nucleating agent, irrespective of the stretching direction. According to Labour *et al.*,[47] the trigonal arrangement of PP chains providing three equivalent glide planes offers a greater probability that favorably oriented crystals will slip and allows a uniform deformation of the β lamellae at reduced yield stress. As a result of the enhanced mobility of crystallites, deformation accompanying phase transformation will easily occur.

When the sample is stretched 45° to the flow direction, the materials behave in a ductile manner for not only PP containing the nucleating agent but also pure PP. Presumably, shear yielding behavior occurs easily in this direction.[48,49]

Thermal expansion originates from the anharmonicity of the potential function, and its anisotropy is always a serious problem for injection-molded products. In general, a material with a high modulus and thus a steep curve of the potential function displays low thermal expansion. As the interaction between neighboring atoms in the same molecule is significantly different from that between atoms in different molecules, oriented polymers always show anisotropic thermal expansion: low in the oriented direction but large in the transverse direction. Among the various parameters used to express thermal expansion, the linear coefficient of thermal expansion β is one of the most conventional parameters. The volumetric coefficient of thermal expansion is expressed by 3β.

Figure 8a shows the linear coefficient of thermal expansion β for pure PP. The average value estimated by $(\beta_{MD}+2\beta_{TD})/3$ is

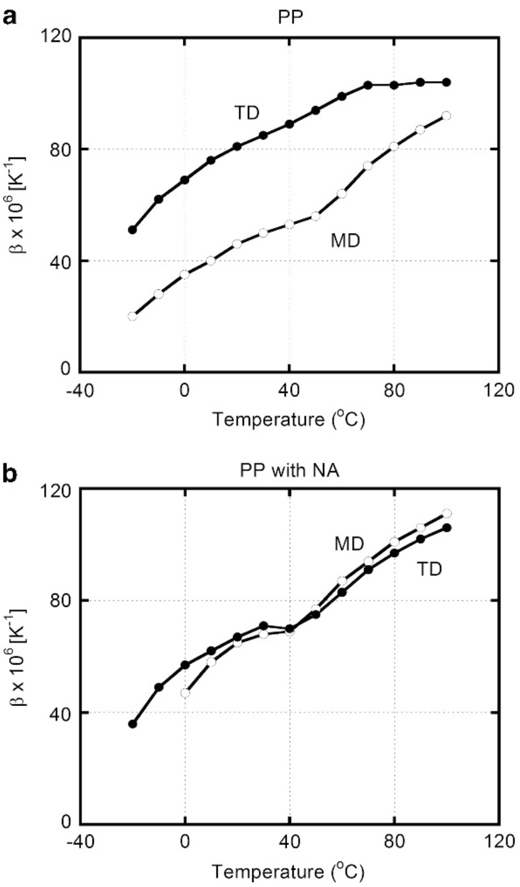

Figure 8 Temperature dependence of linear coefficient of thermal expansion β in machine direction (MD; open symbol) and transversal direction (TD; closed symbol) directions for the injection-molded plates of (**a**) pure polypropylene (PP) and (**b**) PP containing the nucleating agent.

approximately $70\times10^{-6}\,K^{-1}$ at room temperature, which corresponds with that reported in the literature.[50] Moreover, the value for the TD sample is much larger than that for the MD sample. For example, β_{TD} at room temperature is almost twice as large as β_{MD}. The anisotropic behavior in thermal expansion is always detected in injection-molded products because of the marked molecular orientation, which causes a severe problem, especially in large products. On the contrary, there is no significant difference between MD and TD samples for PP containing the nucleating agent, which is reasonable because of the marked perpendicular orientation in the core that offsets thermal expansion in the skin layer. However, the average value is almost the same as that of a conventional PP. It can be concluded that the injection-molded plate of PP containing the nucleating agent is free from anisotropy in not only its mechanical properties but also its thermal properties despite the high level of molecular orientation.

CONCLUSION

The relationship between the structure and mechanical anisotropy of injection-molded PP plates with a unique molecular orientation similar to that of plywood is studied. The orientation direction of PP chains is perpendicular to the flow direction in β-form crystals owing to epitaxial crystallization on the needle-shaped nucleating agent, which is detected in not only the core layer but also the skin layer. On the contrary, the high level of shear stress with rapid crystallization in the skin layer is responsible for the α-form crystals oriented along the flow direction. The α-form orientation is stronger than the β-form, so the skin layer shows MD orientation on average. However, the actual orientation condition in the skin layer is similar to that of woven cloth, cross orientation in perpendicular directions. In the core layer, α-form crystals are also perpendicularly oriented through the crystal growth transition from β-form crystals; the predominant β-form crystals have transversal orientation. Moreover, the sample shows pronounced crystallinity.

The dynamic tensile modulus and Young's modulus in MD are almost similar to those in TD for an injection-molded plate containing the nucleating agent, demonstrating that anisotropy of the modulus is greatly reduced. Furthermore, PP containing the nucleating agent exhibits a higher modulus than pure PP, even in MD stretching, although a large number of the β-form crystals preferentially orient perpendicular to the flow direction. This result will be important in industrial applications because it was previously thought that β-form PP has a low modulus. The high degree of crystallinity is responsible for the enhanced rigidity. As the plate shows an extraordinary molecular orientation with a plywood structure, the anisotropic behavior in thermal expansion, which results in a marked deterioration of the mechanical properties of large products, is also reduced.

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