Plywood-like structure of injection-moulded polypropylene

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ABSTRACT

Injection-moulded products having unique structure, in which the direction of molecular orientation in the skin layer is perpendicular to that in the core layer, are developed employing isotactic polypropylene with a nucleating agent. The extraordinary three-layered structure with β trigonal crystal form in the core layer, which shows higher impact strength than the conventional α monoclinic form, leads to high level of toughness. Moreover, an injection-moulded product having five-layered structure is also demonstrated in this paper. Because of the complicated crack propagation nature due to the abrupt change of molecular orientation, which avoids fractured pieces with sharp-edge, the products with plywood-like structure will be employed in various applications to improve the safety.

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1. Introduction

Plywood is composed of piled wooden sheets in which adjacent plies have their wood grain at right angles to each other for marked strength, resistance of cracks, shrinkage and twisting. The same concept will be applicable to plastic products, because polymer chains orient to one direction in most of conventional plastic products. However, the difficulty of assembling process, leading to poor cost performance, prevents from prevailing the method.

Meanwhile, our research group has clarified that isotactic polypropylene (PP) containing a small amount of N,N′-dicyclohexyl-2,6-naphthalendicarboxamide as a β-modification nucleating agent shows extraordinary molecular orientation at sheet processing recently [1,2]. PP crystallizes on the surface of the needle crystals of the nucleating agent, in which chain-axis (c-axis) of PP orients perpendicular to the long axis of the needle crystals. Since the needle crystals of the nucleating agent align to the applied flow direction by hydrodynamic force, PP chains orient perpendicular to the flow direction at the sheet processing [1]. The anomalous molecular orientation is, however, affected by mixing condition, resin temperature, and cooling condition [2]. In other words, the direction of molecular orientation is adjustable by control of processing conditions. Although the β nucleating ability of N,N′-dicyclohexyl-2,6-naphthalenedicarboxamide was revealed by numerous researchers [3–16], the extraordinary orientation, leading to new application of β crystalline PP, has not been clarified.

In general, injection-moulded products of polymeric materials, including PP, have skin-core structure, in which high level of molecular orientation to the flow direction is attained in a skin layer by flow-induced crystallization [17–22]. On the contrary, a core layer has weak molecular orientation because of low shear rate. In this paper, we developed a novel method to obtain injection-moulded PP having plywood-like structure, considering the difference in crystallization kinetics and applied shear rate between skin and core layers.

2. Experimental

2.1. Materials

Commercially available isotactic polypropylene (PP) (Sumitomo Chemical, FLX80E4, MFR = 10 [g/10min]) was employed in this study. The melting point is approximately 165 °C, because it is a propylene homopolymer. Further, the stereoregularity is more than 95% [mmmm%, pentads], and the weight average molecular weight is approximately 209,000, as mentioned in detail in the preceding paper [2].

PP with 0.05 wt% of N,N′-dicyclohexyl-2,6-naphthalenedicarboxamide (New Japan Chemical, NJ Star[TR] NU-100) were extruded by a corotating twin-screw extruder (Technovel, KZW15TW-45MG-NH) either at (1) 200 °C (sphere) or (2) 280 °C (needle) to control the shape of the nucleating agent [1,2]. The temperature profile in the extruder

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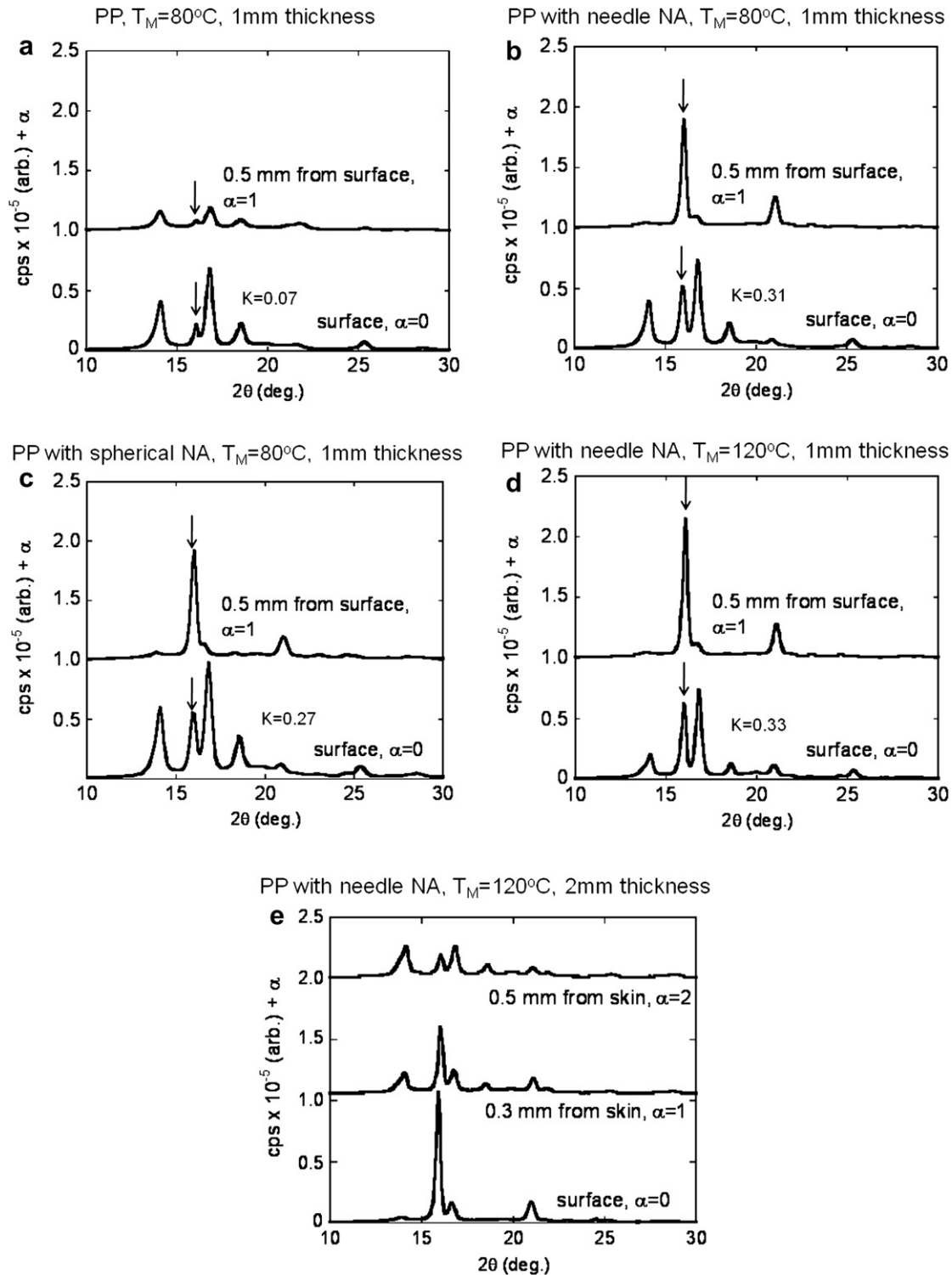[1] Present address Nitta Corp.

Fig. 1. Wide-angle X-ray diffraction patterns for injection-moulded plaques; (a) Pure PP without the nucleating agent, 1 mm thickness, $T_M = 80\ °C$; (b) PP with 500 ppm of the needle nucleating agent, 1 mm thickness, $T_M = 80\ °C$; (c) PP with 500 ppm of the spherical nucleating agent, 1 mm thickness, $T_M = 80\ °C$; (d) PP with 500 ppm of the needle nucleating agent, 1 mm thickness, $T_M = 120\ °C$; and (e) PP with 500 ppm of the needle nucleating agent, 2 mm thickness, $T_M = 120\ °C$. In the figure, the arrow indicates (110) diffracting plane of β form. The K values are also shown.

was as follows; (1) (C1/200 °C, C2/200 °C, C3/200 °C, C4/200 °C, C5/ 200 °C, C6/200 °C, and D/200 °C) and (2) (C1/200 °C, C2/220 °C, C3/ 280 °C, C4/280 °C, C5/280 °C, C6/280 °C, and D/280 °C). The screw rotation speed was 250 rpm, and the out-put rate was approximately 4.0 kg/h. The diameter of the screw was 15 mm and the length-to-

diameter ratio was 45. Prior to melt-mixing, all materials were mixed in a solid state at room temperature and fed into the hopper feeder. Then the extruded strands were immediately quenched in a water bath and then cut by a strand cutter. Injection-moulded plaques (35 mm in width and 40 mm in length) with a thickness of 1.0 and

2.0 mm were prepared by an injection-moulding machine (Nissei Plastic Industrial, PS40E5ASE). The temperature of the mould T_M having a film-gate was controlled at either 80 or 120 °C. The injection-moulding was carried out at the following conditions; the 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, injection-time 20 s, cooling time 30 s, and screw rotation speed 100 rpm. It should be mentioned that it was impossible to obtain a plaque without the nucleating agent when $T_M = 120$ °C because of prolonged crystallization of PP.

Since the injection-moulding was carried out by a conventional method, the molecules in the skin layer are under high shear rate and quenched promptly as compared with those in the core layer.

2.2. Measurements

Wide-angle X-ray diffraction (WAXD) measurements were performed at room temperature using a powder X-ray diffractmeter (Rigaku, RINT2500) by refractive mode. Samples were mounted directly into the diffractmeter. The experiments were carried out using Cu Kα radiation operating at 40 kV and 30 mA at a scanning rate of 1°/min over 2θ(Bragg angle) range from 10° to 30°. In this study, the surface of the plaque, i.e., the skin layer, was measured at first. Then, the skin layer was removed by grinding the plaque in water, and the surface of the grinded product was measured in order to investigate the crystalline form of the inside of the plaque.

Orientation birefringence was measured by using a polarized microscope (Leica, DMLP) with a tilting compensator. Film specimens with 10 μm thickness were cut out by an ultra-microtome (Leica, FCS) at −100 °C parallel to either MD–TD or MD–ND planes.

The impact tests were carried out by a Dupont impact tester (Yasuda Seiki Seisakusyo, Dupont Impact Tester) at room temperature following JIS K 5600. The sample plaque was sandwiched between a spherical punch with a radius of 12.7 mm and a stand having a concave with the same dimension as the punch. A weight was fallen onto the punch from a specified height.

3. Results and discussion

3.1. Crystalline form of PP

Because PP exhibits polymorphic modifications primarily depending on the crystallization condition and the doping of nucleating agents, the crystalline form has to be clarified in detail to understand the mechanical properties. In general, α monoclinic form, that is the most stable one, and β form are dominant in a conventional product. Furthermore, the β form crystal has been focused these days, because it has been known to enhance the impact strength of PP [5,23–25]. Although there have been controversial arguments on the crystalline structure of β form, it was solved in the 1990s by Meille et al. [26] and Lotz et al. [27,28]. According to them, the geometry of unit cell is trigonal containing three isochiral helices with the following parameters: $a = b = 1.101$ nm and $c = 0.65$ nm. In this experiment, not only the surface but also the inside of the plaques was investigated by grinding to remove the surface area of the plaque. Since WAXD measurements were performed by refraction mode, the crystalline form of the inside of the plaque as well as the skin layer was examined by this method. The penetration depth x of X-ray can be estimated by a linear absorption coefficient μ as follows [29];

$$I(2\theta)/I_0(2\theta) = 1 - \exp\left[-\frac{2\mu x}{\sin\theta}\right] \quad (1)$$

where I and I_0 are the intensities of transmitted and incident beams, respectively.

The value of μ can be calculated from the sum of mass attenuation coefficient and given to be 0.0352 m^{-1} for PP [30]. Therefore, about 70% of the diffraction peaks in this experiment is composed of the contribution from the surface area in which the thickness is smaller than 100 μm.
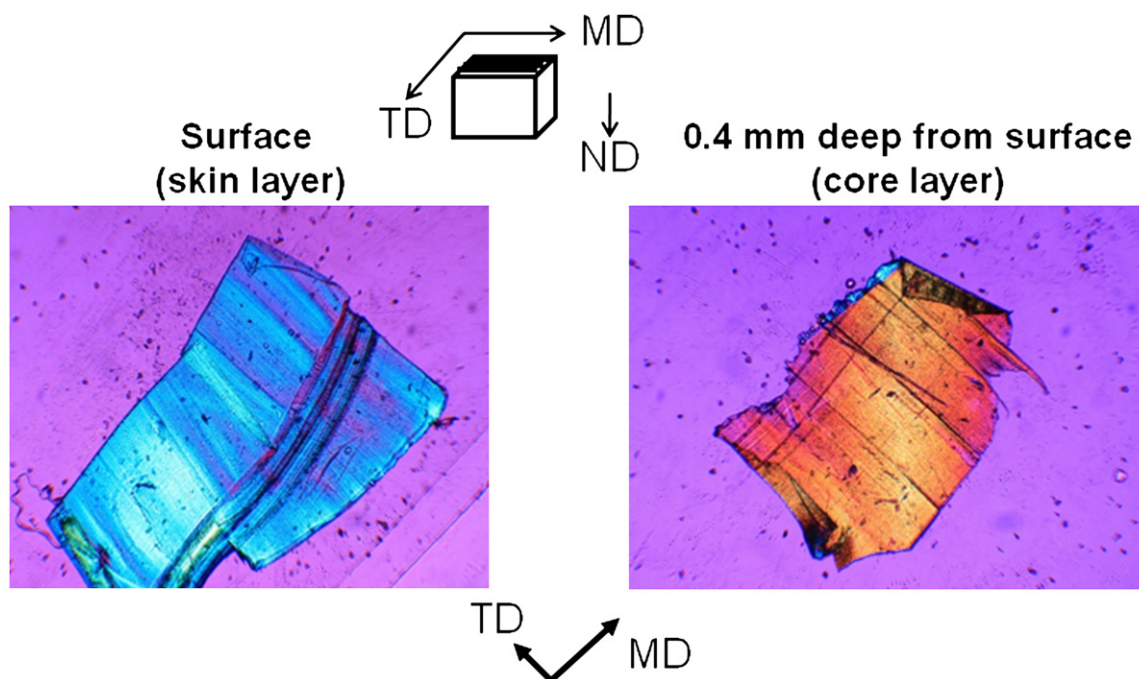

Fig. 2. Optical micrographs under crossed polars inserting a full-wave plate for the slices (MD–TD plane) from the plaque with 1 mm thickness, obtained at $T_M = 80$ °C, for PP containing the needle nucleating agent; (left) surface and (right) 0.4 mm deep from the surface.

In our preceding study, the detailed characterization by two-dimensional wide-angle X-ray diffraction was carried out employing an extruded sheet sample with extraordinary molecular orientation [1]. However, in this study, the X-ray measurements were performed only by the simple refractive mode, because the structure changes in the thickness direction drastically as demonstrated by numerous researchers [20,21,31—33].

Fig. 1(a) shows WAXD profile of the plaque with 1.0 mm thickness for pure PP, obtained at $T_M = 80$ °C. As seen in the figure, the peak ascribed to β trigonal crystals, i.e., $2\theta = 16.1°$, is significantly weak. On the contrary, α monoclinic form is detected dominantly in the skin layer. Further, α form is observed also in the core layer, although the intensities are weaker than those in the skin layer. Moreover, in case of the plaques for the sample containing 500 ppm of needle crystals of N,N′-dicyclohexyl-2,6-naphthalenedicarboxamide, α form is prevailing in the skin layer with sporadical occurrence of β trigonal crystals, as shown in Fig. 1(b), suggesting that N,N′-dicyclohexyl-2,6-naphthalenedicarboxamide shows weak nucleating ability in the skin layer. This is reasonable because β form is generated at specific cooling conditions such as temperature (100—140 °C) and flow field [22,27,28,34—36]. In the current processing condition, intense shear flow in the skin layer leads to α crystalline form, which is a similar result obtained by Scudla et al. [8,9]. On the contrary, strong peaks ascribed to β form are detected in the core layer (0.5 mm from the surface). These results suggest that the nucleating agent acts efficiently in the core layer as similar to the sheet processing [1,2]. The WAXD profile of the sample containing 500 ppm of the spherical nucleating agent, as shown in Fig. 1(c), is found to be almost identical to that in Fig. 1(b), suggesting that the shape of the nucleating agent does not affect the crystalline form of PP to a great extent. A similar WAXD profile is detected for the plaque obtained at $T_M = 120$ °C as shown in Fig. 1 (d). The profile is, however, dependent on the thickness of the plaque. In the thick plaque ($T_M = 120$ °C), as illustrated in Fig. 1(e), β form crystal is dominant in the surface area. Because of low shear rate, β form crystals are generated dominantly even near the surface of the thick plate. On the other hand, α form, that is favourably generated above 140 °C [27,28,34—36], appears in the core layer, because cooling rate in the centre area is considerably depressed. This is reasonable because the solidified polymer near the mould acts as a thermal insulator. As a result, N,N′-dicyclohexyl-2,6-naphthalenedicarboxamide loses the nucleating ability of β crystal in the core region at the processing condition.

The crystalline form of PP is always discussed in terms of K value defined as eq. (2), proposed by Turner Jones et al. [37].

$$K = \frac{I_\beta}{I_{\alpha 1} + I_{\alpha 2} + I_{\alpha 3} + I_\beta} \qquad (2)$$

where I_β is the intensity of the peak for (110) diffracting plane of β form and $I_{\alpha 1}$, $I_{\alpha 2}$, and $I_{\alpha 3}$ are those for (110), (040), and (130) planes of α form. Although the fraction of β form is too high to evaluate by eq. (2) for most samples, the skin layer of the plaques with a thickness of 1 mm can be compared using the K value, which is denoted in the figures. It is found that the K value of PP is 0.07, whereas those of the plaques containing the nucleating agent are larger than 0.25, suggesting that the nucleating agent leads to β form crystals even in the skin layer.

3.2. Molecular orientation

In order to comprehend the molecular orientation, the orientation birefringence is evaluated using thin sliced films cut out from the plaque containing needle crystals of the nucleating agent, obtained at $T_M = 80$ °C. Fig. 2 shows the optical micrographs under
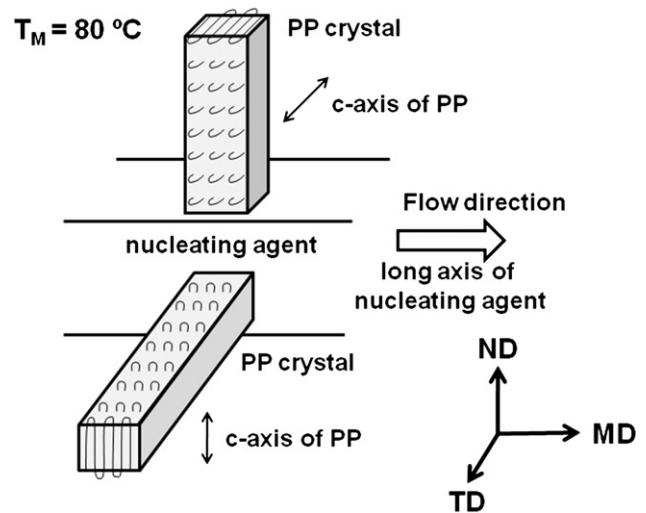

Fig. 3. Schematic illustration of the structure in core layer of the plaque obtained at $T_M = 80$ °C for PP containing the needle nucleating agent.

crossed polars inserting a full-wave plate that adds 530 nm to an optical path. In the figure, MD (machine direction) represents the flow direction and TD denotes the transversal direction. As shown in the figure, the thin slice at the surface is blue, demonstrating that MD is the fast direction, i.e., direction of the molecular orientation. On the other hand, the slice in the core layer (0.4 mm deep from the surface) is yellow. It indicates that TD is the direction of the molecular orientation in the core, which is completely perpendicular to the applied flow field. The values of orientation birefringence measured by a tilting compensator are 1.0×10^{-2} for the surface (left figure) and -1.0×10^{-2} for the core (0.4 mm deep, right figure). The results show that PP crystallizes on the needle crystals of N,N′-dicyclohexyl-2,6-naphthalenedicarboxamide, which orient to the flow direction in the core layer. Since the peculiar growth direction of PP crystals on the nucleating agent, as illustrated in Fig. 3, c-axis of PP orients perpendicular to MD. Furthermore, the pictures demonstrate that the plaque is composed of, at least, three layers (skin/core/skin), in which adjacent layers have molecular orientation at right angles to each other. This type of structure would be obtained for other semicrystalline polymers containing an appropriate nucleating agent with anisotropic shape.

The birefringence distribution of the thin film sliced parallel to the MD—ND (neutral, i.e., thickness direction) plane is indicated in Fig. 4. It is clarified that the orientation direction in the skin layer is
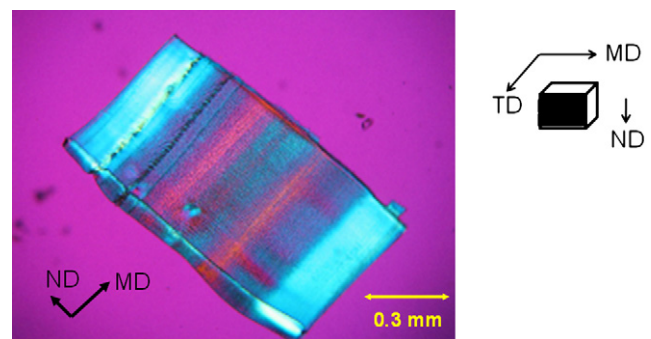

Fig. 4. Optical micrograph under crossed polars inserting a full-wave plate for the slice (parallel to MD—ND plane) from the injection-moulded plaque with 1 mm thickness, obtained at $T_M = 80$ °C, for PP containing the needle nucleating agent.

perpendicular to that in the core. Since the needle crystals are one-axis symmetry, PP chains orient to not only TD but also ND as shown in Fig. 3. The distribution of birefringence in the thickness direction is shown in Fig. 5 employing the samples sliced parallel to the MD—ND plane. In case of pure PP without the nucleating agent, undeformed spherulites are detected in the core layer, suggesting that no orientation occurs on average. As a result, molecular orientation is detected only in the skin layer, which is a typical phenomenon for injection-moulded products. Also in case of the plaque containing the spherical nucleating agent, no orientation is detected in the core as shown in Fig. 5(c), whereas the skin layer is thicker than that of pure PP owing to the prompt solidification. On the contrary, it is confirmed again that the molecular orientation in the core is perpendicular to that of the skin layer for the other samples (Fig. 5(b), (d), and (e)) containing the needle crystals of the nucleating agent. Further, as compared with Fig. 5(b) and (d), the
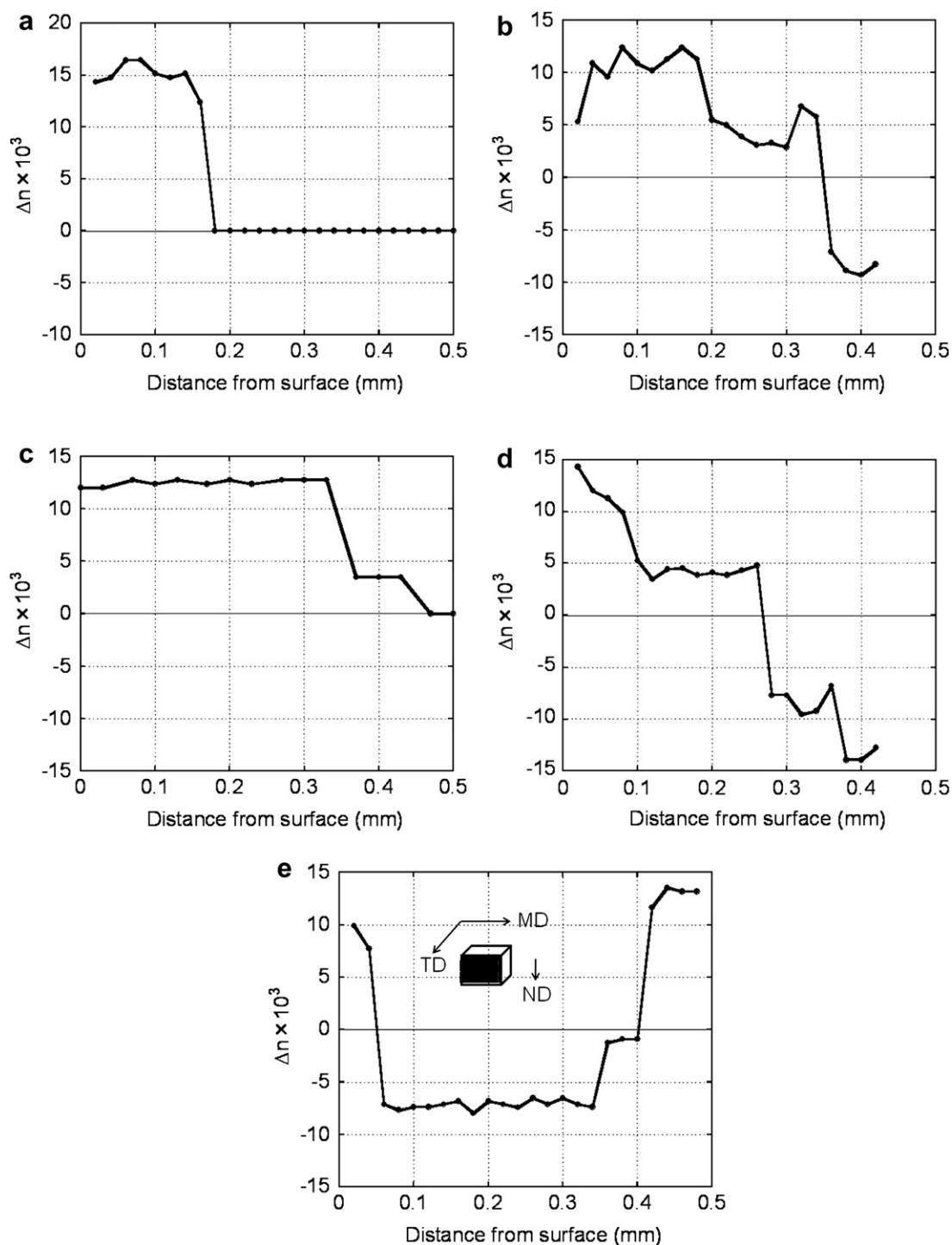

Fig. 5. Distribution of orientation birefringence for the thin slices (parallel to MD—ND plane) of the injection-moulded plaques; (a) Pure PP without the nucleating agent, 1 mm thickness, $T_M = 80$ °C; (b) PP containing the spherical nucleating agent, 1 mm thickness, $T_M = 80$ °C; (c) PP containing the needle nucleating agent, 1 mm thickness, $T_M = 80$ °C; (d) PP containing the needle nucleating agent, 1 mm thickness, $T_M = 120$ °C; and (e) PP containing the needle nucleating agent, 2 mm thickness, $T_M = 120$ °C.

plaque obtained at $T_M = 120$ °C shows large values of negative birefringence because of the thin skin layer. Moreover, it should be noted that the thick plaque for PP containing the nucleating agent ($T_M = 120$ °C), as shown in Fig. 5(e), exhibits unique texture. MD orientation is detected both in the surface and centre regions, whereas PP chains orient perpendicular to the flow direction in the intermediate region. Therefore, the plaque has at least five-layered structure. The MD orientation near the centre area is reasonable for the product, because PP crystallizes in α form as shown in Fig. 5(e). Consequently, PP molecules orient to the applied flow direction.

3.3. Mechanical properties

The effect of plywood-like structure as well as the polymorph on the mechanical properties is studied by Dupont impact test. It is found that Dupont impact strength of the plaque with 1 mm thickness for PP containing the needle nucleating agent, obtained at $T_M = 80$ °C, is approximately 1.20 J, whereas that with the spherical one (no plywood structure) is 1.05 J. The result shows that the plywood-like structure is responsible for the improvement of mechanical toughness to some degree.

Further, it is found that the impact strength of pure PP with K value of 0.07 is found to be 0.45 J. Although the connection between neighbour crystallites should be considered carefully based on the recent study [38], the huge difference in the mechanical toughness between pure PP and PP with the nucleating agent is attributed to the marked toughness of β crystalline structure. Considering that K values of the plaques containing the nucleating agent are more than 0.25 irrespective of the shape of the nucleating agent, the energy dissipation mechanism during yield process, where the phase transformation from β to α form occurs, plays an important role on the mechanical toughness [5,23–25].

Furthermore, the plywood-like structure provides the extraordinary failure behaviour, which is marked for the plaque with 2.0 mm thickness, as shown in Fig. 6. The crack along to the flow direction is detected at the surface attached to the stand with a concave. Further, in the core region, the crack along to TD is detected. On the contrary, the other side of the plaque attached to the spherical punch has no crack. The results indicate as follows; (1) the crack propagation, initiating at the surface, is prohibited inside the plaque because of the abrupt change of the molecular orientation, and (2) another crack whose propagation direction is perpendicular to the initial one is generated inside of the plaque. The complicated crack propagation mechanism, leading to the
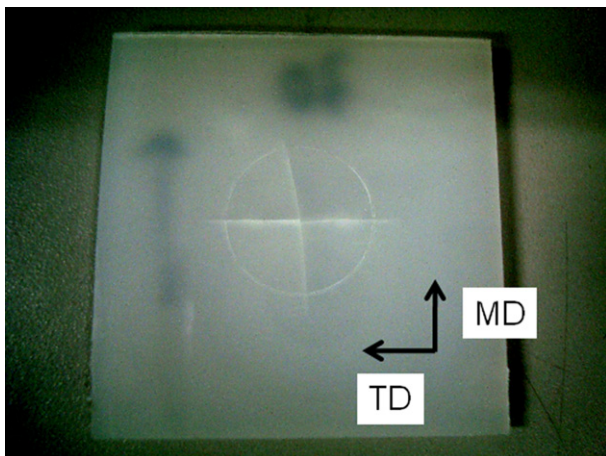
control of the shape of the broken pieces, will have an intense impact on various applications, because broken pieces without sharp-edge are responsible for the safety, for example, in case of automobile parts and housing parts of home electric appliances.

4. Conclusions

The structure and mechanical properties of injection-moulded plaques having plywood-like structure are studied employing PP containing a small amount of *N,N'*-dicyclohexyl-2,6-naphthalenedicarboxamide as a β form nucleating agent. In the injection-moulded plaque, PP chains align to the flow direction with a large amount of α monoclinic crystals in the skin layer owing to the flow-induced crystallization. On the contrary, the orientation direction of PP chains in the core layer is perpendicular to the flow direction owing to the peculiar crystallization from the surface of the needle crystals of the nucleating agent, which aligns to the flow direction by the applied hydrodynamic force. Moreover, the mechanical toughness of the plaques is improved greatly because of the following two reasons; (1) large fraction of β form crystals of PP and (2) propagation direction of a crack changes abruptly inside the plaque because of the plywood-like structure. Since the plywood-like structure could control the shape of fractured pieces without sharp-edge as well as the enhancement of the mechanical toughness, it will be employed in industries to improve the safety of products.

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Fig. 6. Sample specimen after DuPont impact test. The plaque containing the needle nucleating agent was obtained at $T_M = 120$ °C. The thickness of the plaque is 2 mm.

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