Perpendicular Orientation of Dispersed Rubber in an Oriented Polypropylene Sheet

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Abstract

An immiscible blend of isotactic polypropylene (PP) and ethylene-butene-1 copolymer (EB) (PP/EB = 70/30) containing a small amount of N,N’-dicyclohexyl-2,6-naphthalenedicarboxamide as a nucleating agent for β-form crystals was prepared by T-die extrusion. We successfully prepared an extruded sheet, in which the orientation of the PP molecules is perpendicular to the deformation of the EB particles; i.e., the β-form crystals of PP are predominantly oriented perpendicular to the flow direction of the sheet plane (the transverse direction, TD), whereas the EB droplets are strongly deformed in the flow direction. It should be noted that the EB barely affects the crystalline form and orientation of PP. This extraordinary structure provides unique mechanical anisotropy. The tear strength in the TD sample is significantly enhanced with the anomalous crack propagation in the machine direction (MD). Moreover, the anisotropy in tensile properties such as Young’s modulus, yield stress, strain at break, and dynamic tensile modulus becomes reduced.

Keywords: polypropylene; ethylene-butene-1 copolymer; T-die extrusion; mechanical anisotropy
Isotactic polypropylene (PP) is widely used in various applications because it is inexpensive and lightweight. In particular, the trend in the automobile industry to use PP will continue because weight reduction is an inevitable future priority. Generally speaking, both rigidity and high impact strength are required for a material design of PP [1]. Therefore, the technology of the blend with rubber [1-17] and fillers [18,19] and the addition of a nucleating agent [20-25] has been intensively studied. Various types of elastomeric materials have been employed as impact modifiers. In particular, after the development of metallocene catalyst, ethylene-butene-1, ethylene-hexene-1, and ethylene-octene-1 copolymers have been preferred for this purpose, because they have low interfacial tension with PP compared with traditional ethylene-propylene copolymers. Such miscibility and/or compatibility have been predicted by the difference in statistical segment length [1,12,17] and packing length [8,14,17], and have been summarized from the perspective of the species and content of the \( \alpha \)-olefin [2,3,7,15]. The rheological properties [4,5,9], crystallization behavior [6,16], and processability [10,11] of PP blends with ethylene-\( \alpha \)-olefin copolymers have also been elucidated. Accordingly, controlling the particle size of a rubber dispersion in a PP continuous phase improves the mechanical properties of the material. In general, low interfacial tension, and viscosity matching between components enable the formation of small particles with uniform dispersion by melt blending. Furthermore, the nucleation process of PP plays a key role in the processing operation because its mechanical properties are largely dependent on the form and degree of crystallinity. As well known, PP has various crystalline forms such as monoclinic \( \alpha \) modification, trigonal \( \beta \) modification, orthorhombic \( \gamma \) modification, and
smectic form, which are determined by crystallization conditions and additives [2,3,7,8,12,14,17]. Of all the crystalline structures, recent attention has focused on β-form crystals owing to the development of highly efficient nucleating agents such as 1,3,5-benzenetrisamide [26] and N,N’-dicyclohexyl-2,6-naphthalenedicarboxamide [27,28]. These nucleating agents enhance the modulus, which was considered one of the unfavorable properties of β-form crystals. Moreover, a recent report on the enhancement of the melting point using β-form crystals [29] should encourage the industrial applications.

N,N’-dicyclohexyl-2,6-naphthalenedicarboxamide has been used to ensure the molecular orientation of the PP chains in the transverse direction (TD) [30-35]. Under suitable processing conditions, the nucleating agent appears as needle-shaped crystals in PP, and is aligned with the direction of flow by hydrodynamic force. Owing to the unique crystallization behavior of PP, in which the c-axis of the PP crystals grows perpendicular to the long axis of the needle-shaped nucleating agent by epitaxial crystallization, the PP chains orient perpendicular to the flow direction during T-die extrusion [31]. The resulting product has unique mechanical properties. Orientation control using nucleating agents is applicable to injection-molding. The peculiar orientation of the PP chains, i.e., in a plywood-like structure, prohibits crack propagation and reduces anisotropy in modulus and in thermal expansion [32,35]. A combined approach involving the addition of rubber and the control of orientation using a specific β nucleating agent is expected to maximize the mechanical performance of PP. Although several papers have been published regarding polymer blends of PP and ethylene-α-olefin copolymers, there have been few reports describing in detail of PP blends containing a β nucleating agent [36-39].
Furthermore, in industrial applications the molecular orientation of the PP and the rubber dispersion are controlled independently.

The present research focuses on an extruded sheet comprising PP and ethylene-butene-1 copolymer (EB) with the nucleating agent, \(N,N^\prime\)-dicyclohexyl-2,6-naphthalenedicarboxamide. The orientation of the PP molecular chains and the deformation direction of the rubber particles are investigated in detail with an evaluation of the mechanical properties.

**Materials and Methods**

**Materials**

The raw materials used in the present study were: a commercially available isotactic polypropylene homopolymer (PP) (SunAllomer, PM600A, melt flow rate (MFR) 7.5 [g/10 min at 230°C], Mn 63,000, Mw 360,000), and an ethylene-butene-1 copolymer (EB) (Mitsui Chemicals, TAFER DF610, MFR 2.2 [g/10 min at 230°C], density 860 kg/m\(^3\), ethylene content 54 wt.%). \(N,N^\prime\)-dicyclohexyl-2,6-naphthalenedicarboxamide (New Japan Chemical, NJ Star NU-100) was used as a \(\beta\) nucleating agent without further purification.

**Sample preparation**

Melt-mixing of PP with 0.1 wt.% of the \(\beta\) nucleating agent was performed by a counter-rotating twin-screw extruder (Technovel, KZW15TW-45MG-NH) with 0.05 wt.% of 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate (Ciba, Irganox 1010) and 0.1 wt.% of tris(2,4-di-tert-butyl-phenyl)phosphate (Ciba, Irgafos 168) as thermal stabilizers,
and 0.05 wt.% of calcium stearate (Nitto Kasei Kogyo) as a neutralizing agent. The screw diameter of the extruder was 15 mm and the length-to-diameter ratio was 45. The machine was operated at a screw rotation speed of 250 rpm. The mixing was performed at 260°C to completely dissolve the nucleating agent in molten PP. The extruded strands were dipped in a water-bath and cut into pellets approximately 2.3 mm in diameter.

The pellets of PP containing the nucleating agent and EB were fed into a single-screw extruder (Technovel, SZW25GT-28VG-STD) equipped with a T-die (300 mm wide with a 0.5 mm die lip) at a blend ratio of 70/30 (PP/EB) by weight. The output rate was 3 kg/h. The screw diameter and the length-to-diameter ratio were 25 mm and 28, respectively. The speed of screw rotation was 40 rpm. The sheet was stretched in the air gap (10 mm) between the die lip and the chill roll. The temperatures of the die and chill roll were maintained at 200°C and 103°C, respectively. The diameter of the chill roll was 250 mm and the rotational speed was 1 rpm. Reference samples comprising extruded sheets of PP containing the nucleating agent and PP/EB without the nucleating agent were also prepared under conditions identical to those described above.

Measurements

Thermal analysis was conducted using a differential scanning calorimeter (DSC) (Perkin Elmer, DSC 8000) under a nitrogen atmosphere to avoid thermal-oxidative degradation. Samples weighing approximately 3 mg were sealed in aluminum pans. The melting and crystallization profiles were recorded at a heating rate of 10°C min⁻¹ and a cooling rate of 10°C min⁻¹.

The temperature dependence of the dynamic tensile moduli of the extruded sheets was measured between -80°C and 175°C using a dynamic mechanical analyzer.
(UBM, Rheologel-E4000-DVE). The frequency was 10 Hz and the heating rate was 2°C min⁻¹. The extruded sheet was cut into small rectangular pieces, 5 mm wide and 20 mm long, that were mounted between gauges with a distance of 10 mm. The measurements were carried out on two types of sample to investigate the mechanical anisotropy: one was cut parallel to the flow direction (the machine direction (MD) sample), and the other was perpendicular to the flow direction (the transverse direction (TD) sample). In the case of the MD sample, the direction of the applied oscillatory strain coincided with the flow direction.

To analyze the orientation and crystalline form of the PP molecules, wide-angle X-ray diffraction (WAXD) patterns were collected using a high-speed two-dimensional X-ray detector (Rigaku, PILATUS 3R 100K). The measurements were carried out using CuKα radiation operated at 40 kV and 30 mA with a scanning range of 20° (the Bragg angle) from 10° to 30°. Small pieces of the sample (approximately 1.0 mm thick) were mounted on the diffractometer. The X-ray beam was irradiated normal to the MD-ND plane (edge view: EV) and the MD-TD plane (through view: TV). For the EV measurements, ten sheets of the sample were laminated with polystyrene solution, whereas only one sheet was used for the TV measurements.

The orientation of the PP lamellae was investigated using a transmission electron microscopy (TEM) (JEOL, JEM-2100FX) at an acceleration voltage of 200 kV. The samples were embedded in epoxy resin and sectioned using an ultramicrotome (RMC-Boeckeler, Ultramicrotome MT-XL) equipped with a diamond knife after exposure to the vapor of ruthenium tetraoxide at 40°C for a day. Cross-sectional specimens (100 nm thick) were cut from the stained sample in the MD-ND plane.
The deformation of the EB dispersed phase was observed by means of a scanning electron microscopy (SEM) (Hitachi, S4100) with an acceleration voltage of 20 kV. For non-conductive samples, the specimens were coated with Pt/Pd alloy for 60 seconds by an ion sputtering machine (Hitachi, E1010). The surface of specimen was removed using a rotary microtome (Yamato Kohki Industrial, RX-860) and immersed in xylene at room temperature for 3 days to elute the rubber particles.

Stress-strain curves were investigated at room temperature using a tensile machine (Tokyo Testing Machine, LSC-05/300) following ASTM D638. The specimens were cut into dumbbell-shaped pieces (10 mm wide and 40 mm long) using dumbbell cutter No.3 referenced from JIS K6251, in which the sample size was reduced by 40%. The initial distance between the gauges was 30 mm, and one of the crossheads was moved up at a constant speed of 10 mm min\(^{-1}\). Stretching was performed in two directions: one was parallel to the flow direction (the machine direction (MD) sample) and the other was perpendicular to the flow direction (the transverse direction (TD) sample). All measurements were performed at least five times, and the average values were calculated. The elongation at break was evaluated by measuring the final gauge length of the narrow part of the dumbbell.

The tear test was investigated by the Trouser method using a tensile machine (Tokyo Testing Machine, LSC-05/300). Two types of sample were cut from the extruded sheet; one had a notch parallel to the flow direction, that is, the machine direction (MD), and the other had a vertical notch, that is, the transverse direction (TD). The specimens were stretched at room temperature at a speed of 200 mm min\(^{-1}\). The distance between the gauges was 20 mm.
Results and Discussion

Characterization of blend sheets

The melting and crystallization behaviors of the extruded sheets are shown in Fig. 1. As shown in Fig. 1a, the pure PP sheet exhibits a main melting peak at 165°C, suggesting α-form crystals with a small shoulder peak of β-form crystals at 150°C. A similar melting profile is observed in the PP/EB sheet. For the sheet containing the nucleating agent, two distinct peaks are detected at 145°C and 151°C, which can be attributed to β-form crystals. Furthermore, a sharp peak due to the α-form crystals appears at a slightly higher temperature than that for pure PP. The recrystallization after melting of thick β-form crystals is responsible for thick lamellae of α-form crystals leading to the enhanced melting point as explained by Phulkerd et al. [29]. The same phenomenon is observed for the PP/EB sheet containing the nucleating agent. Under suitable cooling conditions, an annealed sheet of PP containing the nucleating agent has a melting point due to α-form crystals nearly at 170°C [29].

The crystallization behavior during the cooling process from 200°C is shown in Fig. 1b. There is no significant difference in the exothermic crystallization temperature (ca. 117°C) between the pure PP and PP/EB sheets. After the addition of the nucleating agent, the crystallization peak shifts to a higher temperature at 128°C in both the PP and PP/EB sheets. In this experiment, the crystallization temperature of PP is barely affected by EB irrespective of the addition of the nucleating agent, which also indicates that EB particles hardly affect the nucleating ability of the nucleating agent.
Fig. 2 shows the X-ray diffraction curves in the equatorial direction of the MD-TD plane, which are transformed and corrected using Lorentz and polarization (Lp) factors. Both α- and β-form crystals are detected but the β-form crystals are predominant in the sheets containing the nucleating agent. In the sheets without the nucleating agent, the strong peak ascribed to the α-form crystals are detected, although β(110) and β(111) peaks are still confirmed. Relatively high cooling temperature (the chill roll was maintained at 103°C) induces the β-form crystallization to some extent. The XRD patterns also suggest that the addition of EB to PP has a negligible effect on crystal formation. Furthermore, there is an indication that the crystallinity of EB is significantly low in the extruded sheets, because both (110) and (200) planes, which are attributable to polyethylene crystals, are absent.

[Fig. 2]

Fig. 3 shows the 2D-WAXD patterns of the extruded sheets, obtained by directing the X-ray beam in the normal direction for the edge view and in the transverse direction for the through view. The α-form crystals in the pure PP show weak orientation, as seen in Fig. 3a. The diffraction patterns of the PP/EB sheet (Fig. 3b) are almost identical to those of the PP sheet, in which a diffraction peak attributed to the (040) plane of the α-form crystals is detected in the equatorial direction, demonstrating that the PP molecular chains are oriented in the MD direction. For the PP sheet containing the nucleating agent (Fig. 3c), the PP chains in the β-form crystals were oriented in the TD direction. Such molecular orientation is also detected in the PP/EB sheet containing the nucleating agent, in which distinct arcs ascribed to (110) reflection of the β-form crystals
are observed as shown in Fig. 3d. This result demonstrates that PP chains preferentially orient perpendicular to the flow direction. It also indicates that the nucleating agent promotes the growth of β-form crystals with the TD orientation of the PP molecular chains, irrespective of the presence of EB.

![Fig. 3](image)

Fig. 4 shows a TEM image of a thin slice of the TD-ND plane cut from the PP/EB sheet containing the nucleating agent. Phase-separated morphology is clearly seen in this sample, in which the dark region is the EB phase. Furthermore, the crystalline lamellae of PP are detected in the matrix as white lines, which preferentially orient along the ND. Therefore, the growth direction of the PP chains is perpendicular to the ND, i.e., the TD orientation, which corresponds well with the XRD patterns. The compressed stress applied during the chill roll process is responsible for the preferential TD orientation of PP chains, not the ND orientation. The slight deformation of EB particles to the TD would be also attributed to the compression stress at the chill roll, although the deformation of EB particles will be explained in detail later. Furthermore, PP lamellae are incorporated into EB phase, which will provide the strong adhesion between them. This phenomenon is attributed to the low interfacial tension between PP and EB, leading to large interphase thickness in the molten state.

![Fig. 4](image)

Fig. 5 shows SEM images for the PP/EB sheet containing the nucleating agent.
The dark regions are attributable to the elongated pores formed by elution of the EB particles with xylene. As seen in Fig. 5a, the numerous pores are mainly deformed in the flow direction. The length of the pores is found to be approximately 3.0 μm and the diameter is about 0.5 μm. On the other hand, a slight deformation in the TD direction with an averaged pore size of 1.0 μm for the length and 0.5 μm for the diameter is detected in the TD-ND plane, owing to the pressure applied by the chill roll, which corresponds with the TEM image. The marked difference in the pore size between the MD and TD directions demonstrates that EB preferentially orients in the flow direction. This is understandable because the elongational stress in the air gap as well as the shear stress in the die deform the EB particles in the flow direction by the hydrodynamic force. Similar SEM images were obtained for the PP/EB sheet without the nucleating agent (but they are not presented here). This suggests that the nucleating agent hardly affects the rubber dispersion and deformation.

Mechanical properties

Because the molecular orientation of PP is different from that of EB, the sample sheet exhibits anomalous mechanical properties. Fig. 6 shows the dynamic mechanical properties of extruded sheets employing two specimens to apply the oscillatory stain in the different directions, i.e., the machine direction (MD) and transverse direction (TD). As seen in Fig. 6a, both the MD and TD samples for the pure PP sheet show almost the same dynamic tensile moduli over the whole range of temperature. A similar behavior is also detected in the PP/EB sheet, in which PP molecules orient to the flow direction. Since
the molecular orientation is weak, no obvious mechanical anisotropy is observed for the sample sheets without the nucleating agent. Moreover, $E'$ in PP/EB falls off markedly around 165°C which is attributed to melting of $\alpha$-form crystals. For the PP sheet containing the nucleating agent, in contrast, $E'$ in TD is higher than that in MD at low temperatures and vice versa at high temperatures. Based on the mechanical model proposed by Takayanagi et al. [40], the anisotropy of the tie chain fractions, which are deformed in the flow direction by hydrodynamic force during extrusion, is responsible for the crossing behavior in the sample containing the nucleating agent [33]. A similar mechanical behavior is detected for the PP/EB sheet containing the nucleating agent, albeit the crossing behavior is weaker and shifted to the lower temperature region. As compared with the PP/EB sheet, the addition of the nucleating agent enhances $E'$ for the MD sample over a wide temperature range above the glass transition ($T_g$), owing to a high degree of crystallinity resulting from the nucleating effect. Furthermore, a sharp drop of $E'$ is detected around 150°C due to the melting of the $\beta$-form crystals, which corresponds to the DSC and WAXD results. It is found from Fig. 6b that both the PP/EB sheets with or without the nucleating agent exhibit double peaks in the $E''$ curve in the temperature range from -75°C to 40°C; the peak at the higher temperature is attributed to $T_g$ of PP and the other at the lower one is to that of EB.

[Fig. 6]

The stress-strain curves at the strain rate of 0.006 s$^{-1}$ are shown in Fig. 7. The tensile force is applied along the MD or the TD. The difference in the tensile behavior between stretching in the MD and TD is detected in all samples. As seen in Fig. 7a,
pure PP sheet experiences a brittle fracture in the TD stretching beyond the yield point. In the case of MD stretching, however, ductile deformation occurs under a low yield stress. The PP containing the nucleating agent (Fig. 7b) shows high Young’s modulus, which corresponds to the tensile storage modulus. Moreover, yield stress in the MD stretching is greatly enhanced with a ductile manner. The low modulus of EB is responsible for marked decrease in Young’s modulus and yield stress for both the PP/EB and PP/EB containing the nucleating agent as seen in Figs. 7c and 7d. In the PP/EB sheet containing the nucleating agent, the anisotropy in Young’s modulus and yield stress is considerably weaker than that in the PP sheet containing the nucleating agent. The strain at break in the TD stretching for PP containing the nucleating agent is considerably larger than that for pure PP. The ductile behavior is also observed in MD stretching, although the yield stress is high. As a result, the anisotropy of strain at break becomes reduced following the addition of the nucleating agent. The reduction of the mechanical anisotropy becomes more apparent for the blend containing EB, although it is interesting to note that the PP/EB exhibits ductile behavior not only in MD but also in TD stretching. Since the yield stress in TD stretching is lower than that in MD stretching, the deformation of EB particles into flow direction affects the stress-strain behavior greatly, although the deformation behavior of the EB phase is not revealed in this study. The details of mechanical anisotropy in terms of crack propagation are discussed below.

[Fig. 7]

Trouser tear test was carried out at room temperature employing two types of the sheet samples; one has a parallel notch in the flow direction (MD), and the other has a
vertical notch (TD). As seen in Fig. 8a, the pure PP sheet shows higher tear strength in the TD sample. For PP containing the nucleating agent (Fig. 8b), the order is opposite with an enhanced anisotropy in tear strength. In the case of the blend, the tear strength in the TD sample is markedly enhanced, irrespective of the nucleating agent. Furthermore, the direction of crack propagation changes to the MD immediately after the stretching as demonstrated in Figs. 8c and 8d. These results demonstrate that PP orientation has no marked impact on the tear property. The deformation of EB particles plays a dominant role on the tearing. Such information has never been reported before to the best of our knowledge, because the deformation direction of a dispersion is always the same as the molecular orientation direction of matrix in general. Regarding the effect of the nucleating agent, the tear strength of the MD sample is slightly enhanced, although the effect is not as obvious as in the pure PP.

[Fig. 8]

Conclusions

An extruded sheet with unique structure was developed using a blend comprising PP, EB, and a small amount of \(N,N'\)-dicyclohexyl-2,6-naphthalenedicarboxamide. It was found that the nucleating agent promotes the formation of \(\beta\)-form crystals and causes the PP chains orient perpendicular to the flow direction in an extruded sheet, i.e., in the transverse direction, as confirmed by 2D-XRD and TEM characterization. On the contrary, EB is deformed in the flow direction, as revealed by SEM images. As a result, the chain
orientation of the PP molecules is perpendicular to the deformation direction of the EB droplets, which affects the mechanical anisotropy to a great extent. With regard to the tensile properties, the anisotropy in yield stress and strain at break is significantly decreased owing to this peculiar structure. It is proved by the tear test that the strength of the TD sample is increased with a crack growth in the flow direction. This result demonstrates that the deformation of the EB particles in the MD direction exhibits more pronounced effect than the molecular orientation of the PP chains in the TD direction.

References


Fig. 1 DSC profiles of extruded sheets; (a) heating curves and (b) cooling curves.
Fig. 2 Lp-corrected XRD curves obtained from the through view beam for extruded sheets.
Fig. 3 WAXD patterns of the edge views (MD-ND) and the through views (MD-TD) in the samples; (a) PP, (b) PP/EB, (c) PP containing the nucleating agent, and (d) PP/EB containing the nucleating agent.
Fig. 4 TEM image of the TD-ND plane ($\times 15,000$) for PP/EB containing the nucleating agent.
Fig. 5 SEM images of PP/EB containing the nucleating agent. (a) MD-ND plane and (b) TD-ND plane.
Fig. 6 Temperature dependence of dynamic tensile modulus of extruded sheets at 10 Hz; (a) tensile storage modulus $E'$ and (b) tensile loss modulus $E''$. The applied strain was (grey symbol) parallel to the flow direction (MD) and (black symbol) perpendicular to the flow direction (TD).
Fig. 7  Stress-strain curves of (a) PP, (b) PP containing the nucleating agent, (c) PP/EB, and (d) PP/EB containing the nucleating agent at a strain rate of 0.006 s$^{-1}$. 
Fig. 8 Tear-propagation resistance (TPR) versus the applied displacement of notched specimens in MD and TD directions; (a) PP, (b) PP containing the nucleating agent, (c) PP/EB, and (d) PP/EB containing the nucleating agent.