Analysis of Contributing Factors to Production of Highly Transparent Isotactic Polypropylene Extrusion Sheets. Part 2

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To obtain highly transparent isotactic polypropylene (PP) sheet by an industrial process, the influences of the isotacticity and metallocene linear low-density polyethylene (L-LDPE) as crystallization control material were analyzed. The sheet samples were extruded by using a direct single-belt process. Even if the sheeting was carried out under the same conditions, the lower tacticity PP generated the less and the smaller size of spherulites. Low-tacticity PP showed improvement on transparency by heat treatment as well as the high-tacticity PP. Moreover, the behavior of transparency was investigated by 10 wt% addition of various L-LDPE with wide range density. Thanks to the fine distribution particles of L-LDPE in PP matrix, the number of generated spherulites and the growth rate of them were restrained. In the case of addition of L-LDPE with the specific density to PP, the transparency was markedly improved by the heat treatment. According to the density of added L-LDPE, the suitable heat-treatment temperature condition, which showed the best transparency, was changed. This phenomenon could be explained by the refractive index difference of PP matrix and the fine distribution particles of L-LDPE. POLYM. ENG. SCI., 00:000–000, 2011. © 2011 Society of Plastics Engineers

INTRODUCTION

There have been a lot of researches in the past for the higher order of quenched isotactic polypropylene (PP) sheet [1–10]. It is well known that a highly transparent sheet of a crystalline PP resin can be obtained by quick quenching a molten resin sheet in the laboratories. There are mainly two theories in terms of higher-order structure that is formed during its solidification process. One is the crystallization theory of bulk polymers with chain folding based on the nucleation of spherulites and then the growth through the molecular diffusion of spherulites by Hoffman and Lauritzen [11]. Other is a solidification process based on the thermodynamic balance theory of Fischer [12].

There is another theory on the so-called mesomorphic phase generated as a stable intermediate state during induction period of crystallization in the glassy or semi-crystalline states [13–20].

In one of the researches on spherulite nucleation and growth of spherulites, it was reported that PP crystallization is suppressed by rapid cooling, and the volume fraction of small monoclinic structure spherulite in smectic crystalline matrix was found to be ca. 20 vol% by Shibayama et al. [21].

Meanwhile, concerning the solidification process of Fischer, Nitta and Takayanagi [22, 23] proposed the lamellar clustering model with thickness being comparable with the end-to-end chain distance.

On the other hand, on the generation theory of mesomorphic phase, Kaji et al. [24–27] reported that the molten isotactic PP transforms into the mesomorphic phase through a spinodal decomposition type separation when it is quenched below 0°C with a rate faster than 80°C/sec.

There are some articles on the flow-induced crystallization which focused on obtaining highly transparent PP sheet by the industrial extrusion process under the influence of stress rather than the ideal cooling conditions [28–40].

In our previous article, we experimentally conducted the extrusion tests by using many screws with various geometries to obtain a highly transparent PP melt resin sheet before its solidification [41]. The transparency of melted resin sheet was obtained by the screw geometry so that the specific energy consumption was small and the melted temperature was low. Based on these results and
taking a wide applicability for a large size extruder of the production machine into consideration, a screw geometry to satisfy a low external haze and an extrusion stability under higher throughput conditions was designed. Also, to produce a highly transparent PP sheet by an industrial process, as the following process of above mentioned extrusion and melt web section, we analyzed the crystallization behavior of high-tacticity PP under quick quenching and conventional cooling process. We also proposed some guidelines for improvement of transparency [42]. That is to say, the number of spherulites generated decreases and the size of them becomes small by increasing quenching rate. Then, the density difference between spherulite and the matrix domains becomes small by the heat treatment, after forming a mesomorphic phase-type matrix by the quick quenching. In the case of extrusion process, the residual stress is made low, and the stress-induced crystallization should be controlled.

The purpose of this study was to investigate the effects of degree of isotacticity and the addition of metallocene linear low-density polyethylene (L-LDPE) as crystallization control material contributing to transparency.

**EXPERIMENTAL**

Figure 1 shows a schematic diagram of the extrusion process for quick quenching used in the experiments here. A 65-mm diameter single-screw extruder \((L/D = 28)\) and a coat hanger die with 900 mm width and 2 mm lip openings were used. Extruder barrel temperatures were set as follows: C1 (feed), 200°C; C2, 230°C; C3, 250°C; and C4 (metering), 260°C. Die sections were set at 260°C, and all set temperature were kept constant throughout the experiments.

A direct belt system was used for the cooling system. This take-up device was composed of a mirror-finished stainless steel endless belt 0.65 mm in thickness and a mirror-finished roll. Illustrated metal rolls were cooled by a chiller unit. The molten resin sheet, which was extruded from the coat hanger die, was nipped and quenched by the mirror-finished belt and roll with 18°C.

The characteristics of the resin used for the experiment about the influence of isotacticity on the transparency are shown in Tables 1 and 2. The first letters “H” and “L” of sample code express the difference in isotacticity. The higher one is set to H and the lower one is set to L. The code “Q” means quick-quenching process, and the code “A” means annealing, after cooling.

The meso pentad fraction was measured by some precedents 13C-nucler magnetic resonance (NMR) spectroscopy method to go by [43]. The molecular weight distribution was measured by gel permeation chromatography (GPC). The isothermal crystallization time was

<table>
<thead>
<tr>
<th><strong>TABLE 1.</strong> Characterization of polypropylene grades.</th>
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<tbody>
<tr>
<td>PP sheet sample code</td>
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<tr>
<td></td>
</tr>
<tr>
<td>MFR (g/10 min)</td>
</tr>
<tr>
<td>Meso pentad fraction (mol%)</td>
</tr>
<tr>
<td>GPC</td>
</tr>
<tr>
<td>(M_w / M_n)</td>
</tr>
<tr>
<td>Isothermal crystallization times at 125°C (min)</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>L-Q</td>
</tr>
<tr>
<td>3.0</td>
</tr>
<tr>
<td>92.5</td>
</tr>
<tr>
<td>8.45</td>
</tr>
<tr>
<td>35.9</td>
</tr>
<tr>
<td>5.7</td>
</tr>
<tr>
<td>H-Q</td>
</tr>
<tr>
<td>3.0</td>
</tr>
<tr>
<td>97.9</td>
</tr>
<tr>
<td>8.11</td>
</tr>
<tr>
<td>35.3</td>
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<tr>
<td>1.2</td>
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<table>
<thead>
<tr>
<th><strong>TABLE 2.</strong> Summary of transparency and higher order structure of polypropylene sheets (sheet thickness 300 μm).</th>
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<tbody>
<tr>
<td>Sample code</td>
</tr>
<tr>
<td>L-Q</td>
</tr>
<tr>
<td>Meso pentad fraction (mol%)</td>
</tr>
<tr>
<td>Sheeting process</td>
</tr>
<tr>
<td>(\Delta H (J/g))</td>
</tr>
<tr>
<td>Crystallinity (%)</td>
</tr>
<tr>
<td>Total haze (%)</td>
</tr>
<tr>
<td>Internal haze (%)</td>
</tr>
<tr>
<td>Outer haze (%)</td>
</tr>
<tr>
<td>Average diameter of spherulites (μm)</td>
</tr>
<tr>
<td>Peak value of (H_v) scattering intensity ((\times 10^{-3})) (–)</td>
</tr>
<tr>
<td>Average correlation length (μm)</td>
</tr>
<tr>
<td>Average long period (nm)</td>
</tr>
</tbody>
</table>
measured by differential scanning calorimetry (DSC). The sheet samples were heated (at 80°C/min) to 230°C, and then the temperature was kept constant at 230°C for 5 min to eliminate the residual crystals. The samples were then cooled (at 80°C/min) to the predetermined crystallization temperature (125°C) till the crystallization was complete. The time to exothermic peak maximum was measured as the isothermal crystallization time.

The melting enthalpy ΔH was also measured by DSC, and the crystallinity Xc of each sheet was determined from the following equation:

$$X_c = \frac{\Delta H}{\Delta H_{PP}} \times 100 \quad (1)$$

where ΔH is the measured melting enthalpy of the analyzed sample, and ΔH_{PP} is the melting enthalpy of the 100% crystalline phase equal to 164 J/g [44].

The list of the metallocene L-LDPE used as crystallization control material is shown in Table 3. These L-LDPE resins have a density range of 898–918 kg/m³ and a melting point range of 90–124°C. These metallocene L-LDPE were blended by 10 wt% into PP (melt flow rate [MFR] 3.0 g/10 min) with 92.5 mol% of meso pentad fraction, respectively. Then, they were extruded and quenched by using the equipment shown in Fig. 1. After heat treatment at 120–140°C, the physical properties of these sheets were measured.

Table: Characterization of metallocene L-LDPE grades as modification materials for transparency.

<table>
<thead>
<tr>
<th>No.</th>
<th>Density (kg/m³)</th>
<th>MFR (g/10 min)</th>
<th>Melting point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LL-1</td>
<td>898</td>
<td>3.5</td>
<td>90</td>
</tr>
<tr>
<td>LL-2</td>
<td>901</td>
<td>2.0</td>
<td>93</td>
</tr>
<tr>
<td>LL-3</td>
<td>902</td>
<td>3.0</td>
<td>98</td>
</tr>
<tr>
<td>LL-4</td>
<td>903</td>
<td>3.8</td>
<td>98</td>
</tr>
<tr>
<td>LL-5</td>
<td>905</td>
<td>3.5</td>
<td>97</td>
</tr>
<tr>
<td>LL-6</td>
<td>907</td>
<td>2.0</td>
<td>100</td>
</tr>
<tr>
<td>LL-7</td>
<td>909</td>
<td>2.0</td>
<td>111</td>
</tr>
<tr>
<td>LL-8</td>
<td>912</td>
<td>2.0</td>
<td>121</td>
</tr>
<tr>
<td>LL-9</td>
<td>918</td>
<td>2.0</td>
<td>124</td>
</tr>
</tbody>
</table>

Light-scattering patterns were measured photographically and photometrically by using Opto-rheometer model HRS-100 (ORC Manufacturing Co., Ltd.). The average size of spherulites was calculated from 2θ_{max} of Hc intensity according to Stein's method [45] as follows:

$$R_0 = \frac{4.09}{\lambda \sin \theta_{max}} \quad (2)$$

where R_0 is the radius of spherulite, λ is the wavelength of incident light, 2θ_{max} is the scattering angle, which indicates the maximum Hc intensity.

Polarizing microscopy was conducted with a Nikon polarized microscope. Wide-angle X-ray diffraction (WAXD) measurement and small-angle X-ray scattering (SAXS) measurement were carried out using model ultra X 18HB (Rigaku Corp.). The powder diffractometer was used with Ni-filtered Cu-Kα radiation (50 kV, 300 mA, and wave length 0.15418 nm). Transmission electron microscopy (TEM) was carried out using Hitachi H800. The thin-sliced sample was treated by RuO_{4}. The refractive index of the sheet sample was measured by using Metricon Model 2010/M Prism Coupler (Metricon Corp.) [46], and each value was the average of five measured values.

RESULTS AND DISCUSSION

**The Influence of the Isotacticity**

In our previous article, we analyzed the crystallization behavior of high-tacticity PP [42]. In this work, the factors for further improvement on the transparency were investigated. To consider the influence on the transparency of isotacticity, PP with 92.5 mol% of meso pentad fraction was compared with the high-isotacticity PP with 97.9 mol%. As shown in Table 1, both PP grades, of which the molecular weight distribution and MFR are almost the same, were chosen to eliminate the influence of other factors as much as possible. On the other hand, the isothermal crystallization time is short, which means that crystallization rate is fast, and the difference in isotacticity appears in Table 1 notably as a difference in the isothermal crystallization times.

Figure 2 shows micrographs obtained by phase-contrast microscopy of cross-section of (a) L-Q, (b) H-Q, (c) L-QA, and (d) H-QA sheet samples. In both L-Q and H-Q sheets, a lot of small spherulites [42] were observed especially near the sheet surfaces. Compared with the higher-isotacticity PP, even if the sheeting was carried out under the same conditions, the lower-isotacticity PP generated less spherulites. As a result of heat-treating these sheets at 140°C, the image of the spherulites in both sheets was obviously weakened. This shows that the difference in the refractive index of matrix and spherulites became very small by the heat treatment.

Figure 3 shows micrographs of the same samples obtained by polarizing microscopy. In both sheet samples, the maltese cross-pattern used to be detected in the case of spherulites could be observed, especially near the sheet surfaces, same as in Fig. 2. In the cases of quick-quenching samples for which big differences were observed by the phase-contrast microscopy, at a first glance, there were no differences (especially regarding the size and number of spherulites) between quenching sheets and annealed samples by polarizing microscopy. It means that there was no big change from the point of view of a birefringence or an optical anisotropy difference between a matrix and spherulites even by the heat treatment of the quick-quenched sheet. This phenomenon was not concerned with their isotacticities.
Figure 4 shows the variation of $V_v$ light-scattering intensity distribution curves for L-Q, L-QA, H-Q, and H-QA. The $V_v$ light-scattering intensity consists of an optical anisotropy ingredient and a density fluctuation ingredient contribution. These data were measured in the direction of the equator where optical anisotropy ingredient contribution was comparatively small. In the cases of both quick-quenching samples, it turned out that these relative intensities were quite small by the heat treatment. In particular, the H-Q sheet sample showed the marked downward tendency of relative intensity and had much effect on transparency by the heat treatment. On the other
hand, the relative intensity itself of L-QA sheet is smaller, and it means that the absolute density fluctuation is smaller than that of H-QA sheet. Anyway, by carrying out quenching and heat treatment, density fluctuation was decreased, and it is thought that transparency was improved as a result.

Figure 5 shows the variation of $H_v$ light-scattering intensity distribution curves for L-Q, L-QA, H-Q, and H-QA sheets. The peak angle of $H_v$ scattering denotes the size of spherical substances, and relative intensity denotes the number of them. Because intensity peaks were clearly observed in the cases of both L-Q sheet and H-Q sheet, existence of spherulites was suggested. Also, this figure shows that the size and number of spherulites did not change substantially, even if both quick-quenched sheets were heat-treated. As observed in Figs. 2 and 3, it turns out clearly that L-Q sheet has markedly smaller numbers and average diameter of spherulites.

The relative intensity is proportional to the square of the difference of the polarizability in the optic axis direction and the polarizability in the perpendicular direction to the optic axis [45, 47, 48]. These results (which show that relative intensity of both sheets were hardly changed by heat treatment) show that the anisotropy of polarizability in spherulites did not become small by the heat treatment.

Figure 6 shows the variation in SAXS intensity distribution curves for L-Q, L-QA, H-Q, and H-QA. An average long period was calculated from a peak position. The scattering image was isotropic, and it means that it was fundamentally a disorderly structure. When both quick-quenched sheets were heated at 140°C, the peak position of relative intensity shifted to the lower scattering angle and increased.

The transparency and higher-order structure of L-Q, L-QA, H-Q, and H-QA are summarized in Table 2. Here, each haze value was the average of five measured values. As shown in Table 2, it turns out that L-Q sheet, which has lower isotacticity, has markedly smaller numbers and average diameter of spherulites. As a result, the obtained sheet has better transparency with low internal haze.

Although the crystallinity of L-QA sheet calculated from the melting enthalpy data of DSC was increased by heat treatment, the size and number of spherulites were almost unchanged. The internal haze of L-QA sheet was
markedly improved by the heat treatment. These phenomena had shown the same behaviors as the higher-isotacticity PP.

It was found that the average correlation length of both sheets calculated by $V_{\nu}$ light-scattering intensity data were decreased by the heat treatment. Each average long period was increased almost twice. Because the sizes of the spherulites themselves do not have big differences by the heat treatment, these increases in average long period suggest that small crystallites of mesomorphic phase in the matrix merge into some larger structure during meso-\(\alpha\) transition process [42].

From above mentioned points, it is considered that the lower-isotacticity PP, with which it is relatively difficult to make chain-folded structures, has slower nucleation and growth rate of spherulites as shown in Table 1. As a result, the internal haze of the lower-isotacticity PP became better than higher-isotacticity PP.

The Influence of Addition of Metalloocene L-LDPE as Crystallization Control Material

In previous work, we examined the influence of addition of L-LDPE into PP to modify the impact strength at low temperature [49]. At that time, it was found that the sheet transparency was improved by the addition of the specific L-LDPE. In the case of PP/L-LDPE = 50/50 blend, the notion of fluctuation-induced nucleation/crystalization was reported [50]. Then, the contribution to the transparency by blend of various metalloocene L-LDPE, which has narrow composition distribution with wide range density, was investigated.

Figure 7 shows the relationship between the density of blended L-LDPE and total haze. These total haze data, which were obtained by quenching and heat treatment at 120\(^\circ\), 130, and 140\(^\circ\)C, were indicated. In the case of the quenched 100\% PP sheet, the total haze was 9.4\% under the same quenching condition as in Fig. 7, and it was 5.3\% after heat treatment. It was clear that, after heat treatment, the transparency of the blended sheets markedly depended on the density of L-LDPE grade. The L-LDPE grades that showed excellent transparency of 2\% or less of the total haze had the density range of 903–905 kg/m\(^3\). The L-LDPE grades with other density range could not achieve the transparency of 2\% or less of the total haze. According to the density of added L-LDPE, the suitable heat-treatment temperature condition that showed the best transparency was changed.

Figure 8 shows the $H_{\nu}$ light-scattering patterns of L-Q sheet and L-Q with 10 wt\% metalloocene L-LDPE (905

![Figure 8](image_url)

**FIG. 8.** $H_{\nu}$ light-scattering patterns for (a) L-Q and (b) L-Q with 10 wt\% L-LDPE (\(\rho = 905 \text{ kg/m}^3\)) sheets.

![Figure 9](image_url)

**FIG. 9.** Micrographs obtained by transmission electron microscopy of TD cross-sections of L-Q with 10 wt\% L-LDPE (\(\rho = 905 \text{ kg/m}^3\)) sheet.
kg/m³) whose transparency was the best. Average diameter of each of these spherulites was 4.7 and 4.1 μm, respectively, and the spherulites’ diameter of the sheet containing 10 wt% L-LDPE became smaller than that of L-Q. The addition of 10 wt% L-LDPE has considerably weakened the relative intensity of the scattering pattern, and it means that the number of spherulites markedly decreased by the addition of L-LDPE into PP.

Figure 9 shows the TEM micrographs of transverse direction (TD) cross-section in the thickness direction of the sheet that contained 10 wt% L-LDPE (905 kg/m³). The darker and more heavily stained regions represent the L-LDPE particles. The average particle size of L-LDPE was about 100 nm or less near sheet surface, and it was about 200 nm at the sheet center. Similar phenomena were reported about the blend of PP and rubber particles. It was suggested that the viscosity ratio (ηr = ηdispersed/ηmatrix) in blend morphology is very important on the dispersed particle size [51, 52]. It is considered that the L-LDPE particles were aggregated at the sheet center section where the stress level was relatively low.

The average diameter of spherulites shown in Fig. 8 was 4.1 μm. Also, the distribution of L-LDPE particles is shown in Fig. 9. Based on these phenomena, it was thought that L-LDPE particles are incorporated into PP spherulites. Moreover, Fig. 8 showed that the number of spherulites remarkably decreased by the addition of L-LDPE into PP. It was considered that the nucleation and growth velocity of spherulites were suppressed by the existence of these L-LDPE particles.

Figure 10 shows micrographs obtained by phase-contrast microscopy of the sheets in Fig. 8, and Fig. 11 shows micrographs obtained by polarizing microscopy of same sample. As already mentioned, lots of spherulites in L-Q sample were observed relatively near the sheet surface. On the other hand, in the case of L-Q with 10 wt% L-LDPE, very few images of spherulites (the maltese cross-pattern was discerned in high-magnification micrograph of Fig. 11) were observed. It corresponded with the dispersion state of L-LDPE particles in Fig. 9. This results supported the result that the addition of 10 wt% L-LDPE considerably weakened the relative intensity of the scattering pattern in Fig. 8.

Although, as above mentioned, the number and size of spherulites remarkably decreased by the addition of L-LDPE into PP, the appearance of the quick-quenching sheet became rather clouded. From this transparency behavior, Fig. 12 focuses on the sheet density and the refractive index. In Fig. 12, typical samples were selected from the various samples in Fig. 7. Figure 12 shows the relationship between sheet density and refractive index for metallocene L-LDPE (898, 905, and 912 kg/m³)-blended PP sheets. These sheets were obtained by quick quenching and then heat treatment at 120, 130, and 140 °C.

It was found that the refractive index was increased linearly to the sheet density by the various heat treatment conditions. The gradients of the approximated curve of each condition were calculated and shown in Fig. 12. Compared with the PP sheet, the higher the density of added L-LDPE were, the larger the gradient of approximation line became. That is, according to the density of added L-LDPE, the rate of change of the refractive index to the sheet density differed.

Figure 13 shows the relationship between “absolute value of refractive index difference” at each heat-treat-
ment temperature and the total haze based on the data obtained from Fig. 12. Absolute value of refractive index difference was determined from the following equation:

\[
\text{‘Absolute value of refractive index difference’} = |R_{PP} - R_{\text{blended}}| \tag{3}
\]

where \(R_{PP}\) is the refractive index of PP sheet after the heat treatment at \(T^\circ\)C, and \(R_{\text{blended}}\) is the refractive index of PP with 10 wt% L-LDPE after the heat treatment at \(T^\circ\)C. Figure 13 shows that the total haze became small despite the density of added L-LDPE, when the absolute value of refractive index difference became small.

Figure 14 shows the relationship between the heat-treatment temperature and the total haze obtained by 10 wt% additions of L-LDPE with 898, 905, and 912 kg/m\(^3\). In the case of the PP sheet with 898 kg/m\(^3\) L-LDPE, the total haze aggravated along with the increase in the heat-treatment temperature. On the other hand, in the case of 912 kg/m\(^3\) L-LDPE addition, it turns out that the total haze improved along with the increase in the heat-treatment temperature. Moreover, the PP sheet with 905 kg/m\(^3\) L-LDPE had minimum value of total haze to the heat-treatment temperature. These phenomena were due to the following factor. The best heat-treatment temperature condition, at which the absolute value of refractive index difference became minimum, differed respectively, and it depended on the density value of the added L-LDPE material.

Figure 15 shows the relationship between the heat-treatment temperature and the absolute value of refractive index difference. Because the crystallization rate of PP material is slower than that of L-LDPE, the change in PP sheet density by the heat treatment is finally larger than that of the L-LDPE-added sheet density. In the case of the PP sheet with 898 kg/m\(^3\) L-LDPE, the refractive index difference got bigger along with the increase in the heat-treatment temperature. On the other hand, in the case of 912 kg/m\(^3\) L-LDPE addition, it turns out that the refractive index difference got smaller along with the increase in the temperature. Moreover, the PP sheet with 905 kg/m\(^3\) L-LDPE had minimum value of refractive index difference to the heat-treatment temperature. As a result, it turns out that the trend pattern of each data was in agreement with Fig. 14.

From the above results, the following can be considered. In the case of 100% PP sheet, the spherulites made
the internal haze aggravation. In the case of the L-LDPE-added sheet, although the number and size of spherulites remarkably decreased, the refractive index difference of L-LDPE particles and PP matrix made the internal haze aggravation. That is, in the case of a blend of PP and L-LDPE, because the L-LDPE particles have different refractive index from PP material, the transmitted light waves are scattered and the sheet becomes cloudy. When the refractive indexes of L-LDPE and PP are approached by the suitable heat-treatment temperature, the cloudy sheet appearance changes to highly transparent appearance, because the degree of light scattering decreases. However, because the sensitivity of the refractive index to the heat-treatment temperature differs in accordance with density of added L-LDPE, the optimum temperature conditions to obtain the best transparency differ.

CONCLUSIONS

To improve further the transparency of an isotactic PP sheet obtained by an industrial extrusion quenching process, the important factors were investigated. Especially, it was clarified that the isotacticy and the mixing of metallocene L-LDPE were very effective for improvement of the transparency of PP sheet.

Even if the sheeting was carried out under the same quenching conditions, the lower-tacticity PP generated the less and the smaller size of spherulites, and the better transparent sheet was obtained. In the case of low-tacticity PP, the improvement behavior on transparency by heat treatment showed the same tendency as the high-tacticity PP. By heat treatment of the quenched sheet, the size and number of spherulites were almost unchanged, and the density fluctuation was decreased. It is considered that the lower-isotacticity PP, with which it is relatively difficult to make chain-folded structures, has slower nucleation and growth rate of spherulites, and as a result, the internal haze became better than higher-isotacticity PP.

Moreover, when metallocene L-LDPE was added into PP, the number of generated spherulites and the growth rate of them were restrained by the fine distribution particles of L-LDPE in PP matrix. In the case of addition of L-LDPE with the specific density to PP, the transparency was markedly improved by the heat treatment of quick-quenching sheets. According to the density of added L-LDPE, the suitable heat-treatment temperature condition that showed the best transparency was changed. Because the sensitivity of the refractive index to the heat-treatment temperature differed in accordance with density of added L-LDPE, the optimum temperature conditions to obtain the best transparency differed. In the case of the L-LDPE-added sheet, the refractive index difference of L-LDPE particles and PP matrix made the internal haze aggravation. Then, the refractive indexes of L-LDPE and PP are approached by the heat treatment, and it can be surmised that the cloudy sheet appearance changes to highly transparent appearance, because the degree of light scattering decreases.

NOMENCLATURE

\[ \Delta H \] Measured melting enthalpy of analyzed sample (J/g)

\[ \Delta \Delta \text{pp} \] Melting enthalpy of the 100% crystalline phase (J/g)

\[ X_C \] Crystallinity (%)

\[ R_0 \] Radius of spherulite (nm)

\[ \lambda \] Wavelength of incident light (632.8 nm)

\[ 2\theta_{\text{max}} \] Scattering angle that indicates the maximum \( H_i \) intensity (rad)

\[ R_{\text{PPI}} \] Refractive index of PP sheet after the heat treatment at \( T^\circ C \) (–)

\[ R_{\text{IPB}} \] Refractive index of PP with 10 wt% L-LDPE after the heat treatment at \( T^\circ C \) (–)

REFERENCES


47. J.J. van Aartsen, ONR Technical Report No. 83, Polymer Research Institute, University of Massachusetts, Amherst, MA (1966).