Highly Transparent Polypropylene sheets controlled by the blending of the third component

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ABSTRACT

Polypropylene (PP) has a good processability and excellent physical properties and can be produced at a reasonable cost. Therefore, it is widely used in our daily lives and also within industry. However, PP is a crystalline resin, so it is difficult to obtain a good transparency. However, a high transparency is necessary for the packaging of goods. To improve the transparency of the PP sheet, the number of spherulites in the sheet has to be reduced. According to our previous research, it was found that the number of spherulites in the sheet was suppressed by blending of a third component such as metallocene catalyzed linear low density polyethylene (L-LDPE).The purpose of our research was to analyze the influence of the addition of L-LDPE to PP on the sheet transparency. Therefore, the cross section of each sample sheet was observed using the phase-contrast and polarizing microscopes and so on. Furthermore, our study observed the growth of spherulites of in PP blends during the quenching conditions, using a high-speed camera. As a result, we found the number of generated spherulites in the third component blend sample was reduced when compared with PP. It was found that the third component blend samples were able to suppress the nucleation velocity of spherulites under the rapid cooling conditions.

1. INTRODUCTION

Polypropylene is used for the packaging of various products. However, it is difficult to be used in the high transparency field due to the characteristics of crystalline resin. It is found that the existence of spherulites generated in the PP sheet greatly affects the transparency. Therefore, it is essential to control the size and the number of the spherulites to obtain high transparency. In a recent study, it was found that the transparency was improved by the addition of metallocene catalyzed linear low density polyethylene in PP as a third component [1]. However, it hasn't been found that L-LDPE affects either the growth velocity or the generation velocity of the nucleus.

Therefore, in this study, we focused on the influence of cooling speed on the size and the number of spherulites. In order to observe the spherulites generation under the various quenching conditions, a phase-contrast microscope and high-speed camera were used and the mechanism of transparency by the addition of L-LDPE was studied. The analysis of the mechanism was investigated to improve transparency by adding a third component.

2. EXPERIMENTAL
2.1 Samples
Isotactic PP and L-LDPE produced by Prime polymer Co., Ltd were used in these experiments. **Table1** shows the resin characteristics of PP and L-LDPE used in this study. **Table2** shows blending ratio of these resins and the internal haze of each sample. These sheets structure was as follows; A is a standard sample, B-1, B-2 and B-3 are the samples

added 5wt%, 10wt%, 15wt% of L-LDPE to PP, respectively. The sheet samples were produced by using the single belt process under the rapid cooling condition of approximately 18℃. The thickness of these samples was about 300μm. The transparency of the L-LDPE blended PP sheets improved, compared with the pure PP.

Table 1 The properties of PP and L-LDPE samples

Resin	MFR(g/10min)	ρ (kg/m^3)
PP	3.5	910
L-LDPE	3.5	905

Table 2   The internal haze data of each sample

Sample	Blending ratio	Internal haze (%)
A	PP=100	5.83
B-1	PP/L-LDPE=95/5	2.91
B-2	PP/L-LDPE=90/10	2.41
B-3	PP/L-LDPE=85/15	3.46

2.2 Isothermal crystallization under slow cooling
In order to study the influence of spherulites generated speed and growth on the various quenching conditions, the isothermal crystallization velocity during the slow cooling condition, which was much slower than the actual sheet production cooling process, was measured. These samples were cut in the cross-section for thickness of about 30μm and the cut samples were put between a slide glass and a cover glass. Then they were heated by hot stage manufactured by Mettler/Toledo. The experimental process is as follows:

1. These samples were held at 180 ℃ for 30min.
2. They were cooled the temperature to 130℃ at the speed of -20℃ per min.
3. In order to observe the state of isothermal crystallization for 15min, the motion pictures were taken every 1min (see Fig. 1).

These photographs were taken by a phase-contrast microscope and a camera manufactured by Nikon. The number and the size of the spherulites were counted and measured from taken pictures. The number of spherulites divided by actual cross-sectional area of the sheet was indicated as number density of spherulites [mm^{-2}].
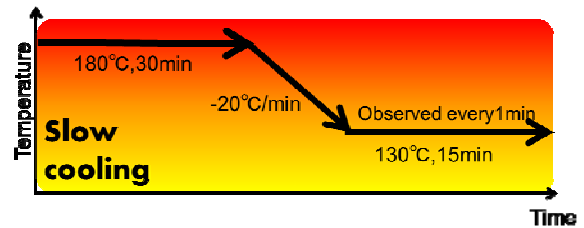

Fig.1 Schematic diagram of the relationship between time and temperature under the slow cooling condition

2.3 Crystallization under rapid cooling
These samples that were cut for fixed size were heated by a hot stage manufactured by Japan High Tech. The experimental process is as follows:

1. These samples were held at 200℃ for 5min
2. They were cooled the temperature to 20℃ at the speed of -45000℃ per min.
3. In order to observe the state of crystallization for 2sec, the motion pictures were taken every 0.002sec during rapid cooling (see Fig. 2).

A high-speed camera manufactured by Keyence was used. In the case of the rapid cooling condition, the number and the size of spherulites were counted and measured from taken pictures.
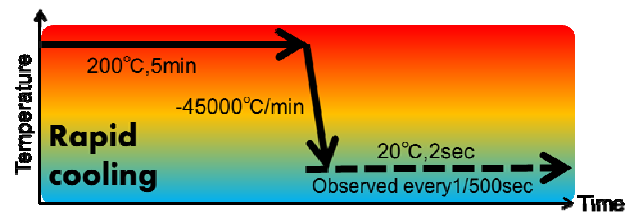

Fig.2 Schematic diagram of relationship between time and temperature under the rapid cooling condition

3. RESULTS AND DISCUSSION
Fig.3 shows the relationship between crystallization time and radius of spherulites under the slow cooling condition. The gradient of this graph means the growth velocity of spherulites. As shown in **Fig.3**, the spherulites grow linearly with crystallization time for any sample. The size of spherulites for all samples hardly changed even if L-LDPE was added into PP. That is to say, the addition of L-LDPE did not affect the growth velocity of spherulites under the slow cooling condition. **Fig.4** shows the relationship between crystallization time and number density under the slow cooling condition. The gradient of this graph means the generation velocity of the spherulites. As shown in **Fig.4**, there is no correlation between PP

and the additive samples. Besides, the number density does not depend on the additive ratio of L-LDPE. As there is no consistent pattern in the data, the influence of generation velocity of spherulites is not be clarified.
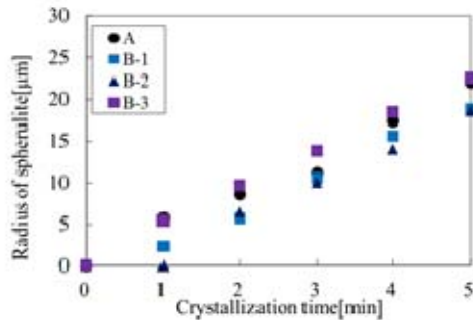

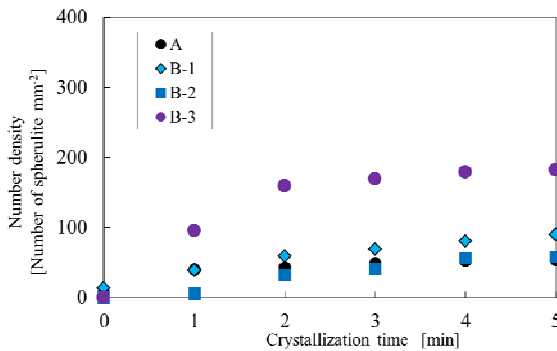**Fig.3 Relationship between crystallization time and radius of spherulites (slow cooling)**

Fig.4 Relationship between crystallization time and number density (slow cooling)

Fig.5 shows the relationship between crystallization time and radius of spherulites under the rapid cooling condition. It can be seen that the radius of spherulites linearly increases with increasing the crystallization time. And These all samples show almost same gradient. Therefore, the growth velocity of spherulites does not change even if L-LDPE is added into PP. This result is similar to the case of the slow cooling. Moreover, a noteworthy result is shown in **Fig.6**. It shows the relationship between crystallization time and number density under the rapid cooling condition. The gradients of the plot in **Fig.6** decreases with increasing the addition ratio of L-LDPE. This consequence means that the addition of L-LDPE decreases the generation velocity of spherulites
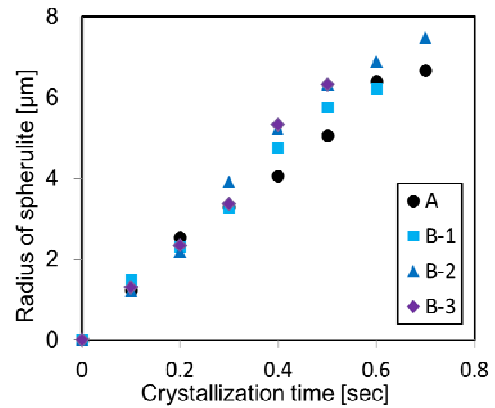

Fig.5 Relationship between crystallization time and radius of spherulites (rapid cooling)
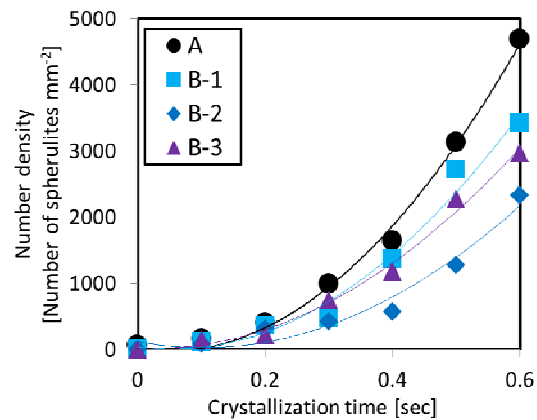

Fig.6 Relationship between crystallization time and number density (rapid cooling)

Because the same phenomenon was seen even if L-LDPE of various conditions was added into PP, it is supposed that the suppressing effect of spherulites generation was obtained by the addition of L-LDPE. These results strongly associate with the internal haze of these sheets. The addition of L-LDPE did not only suppress the generation velocity of spherulites, but also improved the transparency of PP sheet. **Fig.7** shows the relationship between the internal haze and number density under the rapid cooling condition after 0.6 sec. As shown in **Fig.7**, it can be seen that the transparency of PP sheet linearly improves with decreasing the number density. The correlation is very good. As the number of spherulites at the 10wt% addition of L-LDPE is the least number, it can be surmised that the optimum additive ratio exists. This effect was similarly observed in L-LDPE of the other conditions. Now, the reason for a decrease in generation of spherulites is considered. **Fig.8** shows the comparison between the generated spherulites in pure PP (A) and that in the additive sample (B-2). As shown in **Fig.8**, the spherulite in A grows radially and orderly from the

center. In contrast, the spherulite in B-2 grows to the different directions. It seems that the generated spherulite in B-2 has a deformed shape. As the reason, it is inferred that L-LDPE which is dispersed to nano size in PP matrix interferes with spherulites generation. According to the previous study, it is known that the difference of density between PP matrix and L-LDPE particles gives great effect to the transparency of sheet. The density difference of L-LDPE particles and PP matrix made the internal haze deteriorate. In order to add L-LDPE of the same density as PP, it is considered that the good transparency was obtained. Then, it was examined why the cooling rate affected the difference of generation spherulites. The behavior of nucleation generated is different because the cooling rate is different over 1000 times compared with the actual quenching process. It turned out that the generation of spherulites was so sensitive to cooling rate. Summarizing the above results, the addition of L-LDPE whose density is similar to PP density does not affect the growth velocity of spherulites. Whereas, the addition of L-LDPE affects the generation velocity of spherulites.

Fig.7 Relationship between internal haze and number density under rapid cooling

Fig.8 Comparison between the generated spherulites in pure PP (A) and that in the additive sample (B-2)

4. CONCLUSION

The addition of metallocene catalyzed L-LDPE decreased the nucleation velocity of the spherulites in PP matrix and markedly improved the transparency to suppress and interfere the generation of spherulites. On the other hands, the addition of L-LDPE did not affect the growth velocity of spherulites. Additionally, the crystallization behavior of the actual sheet process could be clarified by the rapid cooling experiment.

Reference
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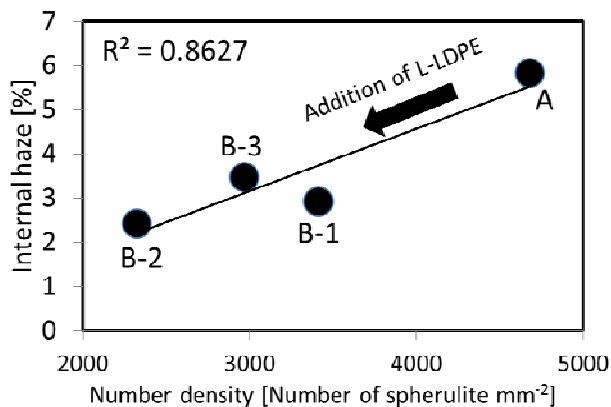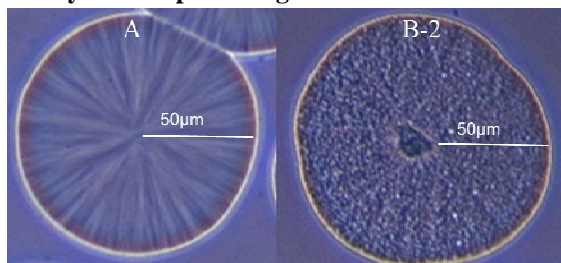4) K.Nitta and M.Takayanagi, J. Macromol. Sci. Phys. B, 42, 107 (2003)