

Structure development of polyethylene film during stretching

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ABSTRACT

Linear low density polyethylene (LLDPE) has high impact strength, high tear strength and high tensile strength. However it has poor stretchability, compared with polypropylene which is widely used as an oriented film. Therefore the purpose of this study was to improve the stretchability of LLDPE film. High density polyethylene (HDPE) and low density polyethylene (LDPE) were blended in order to improve it. HDPE could be stretched at a high temperature and LDPE was expected to make the melt tension stronger. Furthermore, the relationship between stretchability and the higher order structure was investigated. The higher order structure development of LLDPE film during stretching was also observed. In this study, stretchability refers to the stretchable temperature width. As a result, it was found that the stretchability of LLDPE blended with HDPE and LDPE was improved. This was due to the fact that blend HDPE widens composition distribution, and blend LDPE improves the entanglement of the molecular chain. It was also found that the higher order structure that had good stretchability was that of those where crystalline phases existed without melting at high temperatures.

Keywords: LLDPE, stretchable temperature width, the higher order structure

1. Introduction

In recent years, polymer film is essential in our lives. Among them, linear low density polyethylene (LLDPE) has good physical properties, therefore it is now used in the field of film. However, compared with polypropylene (PP) which is same polyolefin as PE, PE can be stretched only in narrow temperature range. For this reason, an oriented PE film isn't widely used in the market. So in this study, high density polyethylene (HDPE) and low density polyethylene (LDPE) were blended to LLDPE to improve stretchable temperature width. The purpose of this study is to design a resin which has wide stretchable temperature width. Furthermore, we studied how the higher order structure of LLDPE film affects stretchable temperature width. By observing the higher order structure development during the stretching, blend effect of HDPE and LDPE was investigated.

2. Experiments

2.1 Samples

In this study, LLDPE having density 920kg/m³ is used as a standard sample, namely LL①. HDPE and LDPE were blended to it. LL② is narrow Mw/Mn sample. DSC, WAXS, SAXS, light scattering, and optorheometer made by ORC manufacturing co.,Ltd were used as experiment devices. Samples name and physical characteristics are shown in **Table 1**.

Table 1 Physical characteristics of LLDPE samples

Samples	Density(kg/m ³)	MFR(g/10min)	Mw/Mn
LL①	920	2.0	4.11
LL①+HD	924	1.9	6.84
LL①+LD	916	2.2	6.22
LL①+HD+LD	925	1.9	7.26
LL②	921	2.0	2.56

2.2 Measurement result

2.2.1 Evaluation of Stretchability

Fig.1 shows the relationship between stress and stretchable temperature. This data was obtained by using Stress-Strain curves of such samples stretched at any temperature with optorheometer. Also stress and stretchable temperature of the time stretched at the stretching ratio 7 were plotted. In order to find stretchable stress width obtained by a production line, the temperature within it was defined as stretchable temperature width. Table 2 shows stretchable temperature range and stretchable temperature width gained from Fig.1 .

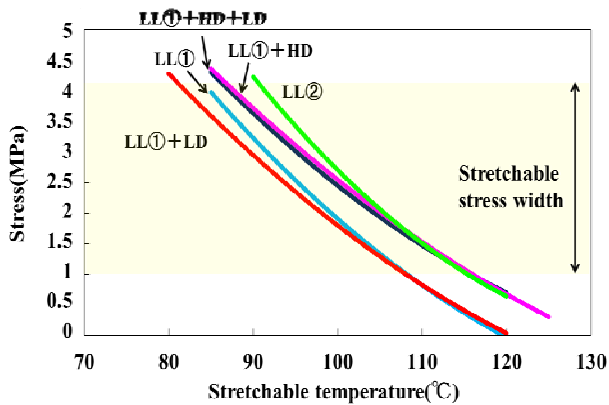


Fig.1 Stress-stretchable temperature

Table 2 Stretchable temperature range and stretchable temperature width

Samples	Stretchable temperature range (°C)	Stretchable temperature width (°C)
LL①	84~108	24
LL①+HD	86~115	29
LL①+LD	81~108	27
LL①+HD+LD	86~116	30
LL②	95~115	20

2.2.2 Evaluation of composition distribution

In the previous study, it was reported that the stretchable temperature width strongly correlates with the composition distribution. Therefore DSC was used to evaluate the composition distribution. Fig.2 shows the relationship between integral ratio of melting component and melting temperature. The integral ratio of melting component is the result endothermic curve of DSC was integrated by the temperature. Also the integral ratio of melting component expresses percentage of a molten resin. Melting temperature range and melting temperature width are obtained from Fig.2 as a half melting condition that 20% ~ 60% is suitable for the stretching. The result is shown in Table 3. Then the stretchable temperature width of Table 2 and

melting temperature width of Table 3 were plotted to evaluate both relationship. It is shown in Fig.3.

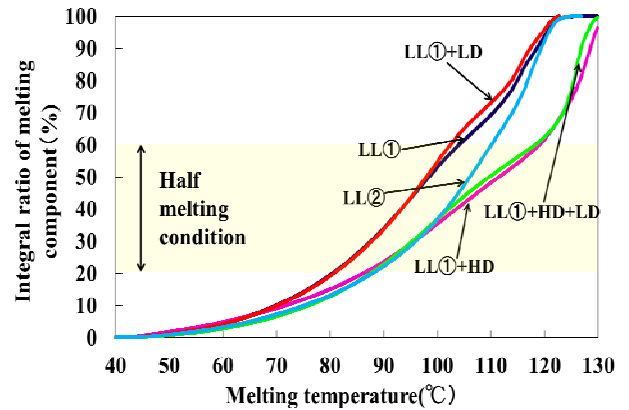


Fig.2 Integral ratio of melting component - melting temperature

Table 3 Melting temperature range and melting temperature width

Samples	Melting temperature range (°C)	Melting temperature width (°C)
LL①	79~107	28
LL①+HD	86~119	33
LL①+LD	82~106	24
LL①+HD+LD	89~119	30
LL②	91~112	21

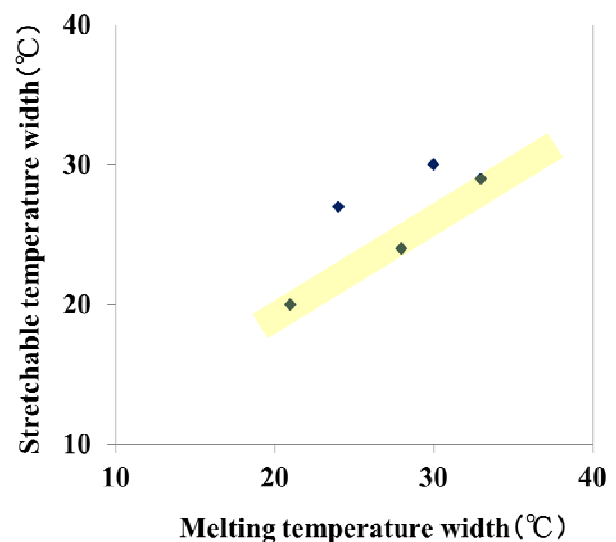


Fig.3 Stretchable temperature width - melting temperature width

2.2.3 Observation of the higher order structure

In order to observe the higher order structure development of LLDPE film during the stretching, the light scattering was used. The result is shown in Fig.4, and Table 4 shows the result that the sizes of spherulites formed in non-stretched sheet were calculated from Hv light scattering images. Additionally, the relationship between stretchable temperature width and the higher order structure was investigated. The results of SAXS rising temperature of LL① and LL①+HD are shown in Fig 5 and Fig 6. The relationship between the degree of crystallinity gained from peak separation and temperature is shown in Fig.7. Table 5 shows the thicknesses of crystalline phases.

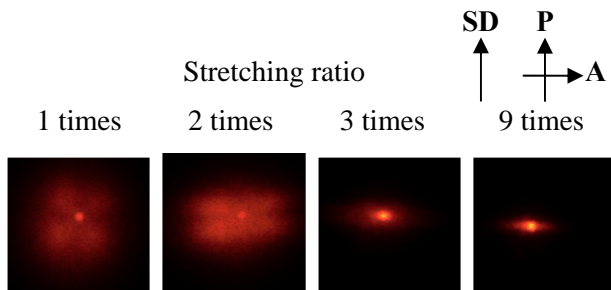


Fig.4 Change of Hv light scattering image during the stretching

Table 4 The sizes of spherulites

Samples	The sizes of spherulites(μm)
LL①	30.0
LL①+HD	5.5
LL①+LD	4.2
LL①+HD+LD	4.2
LL②	41.0

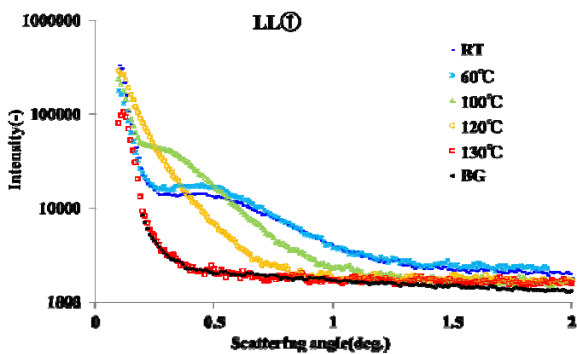


Fig.5 Intensity- scattering angle of LL①

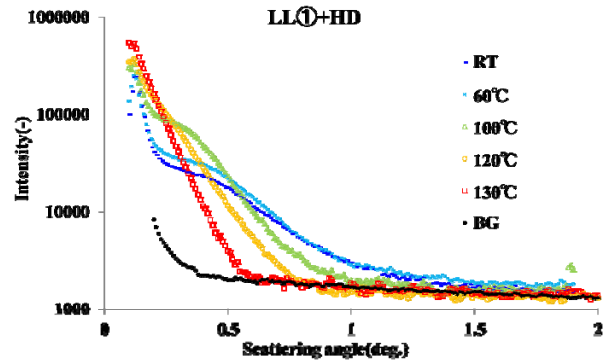


Fig.6 Intensity- scattering angle of LL①+HD

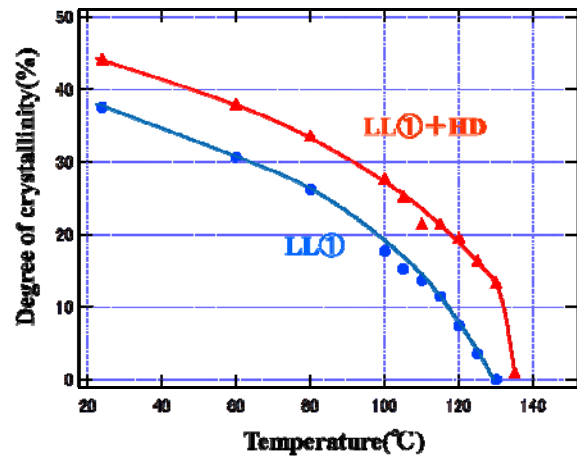


Fig.7 Degree of crystallinity-temperature of LL① and LL①+HD

Table 5 The thicknesses of crystalline phases

Samples	The thicknesses of crystalline phases(nm)
LL①	7.3
LL①+HD	10.5
LL①+LD	7.3
LL①+HD+LD	10.7
LL②	6.5

3. Results and Discussion

3.3.1 The result of evaluation of stretchability

By uniaxial tension test to evaluate stretchable temperature width, stretchable temperature width of LL①+HD+LD was the widest, and the second is that of LL①+HD. From these results, it was found that blending HDPE strongly affected a behavior of the stretching. As this reason, It is considered that blending HDPE makes the stretching at high temperature possible. Stretchable temperature width

of LL①+LD is wider than that of LL①, but LDPE did not affect than HDPE.

3.3.2 The result of evaluation of composition distribution

As shown in **Table 3**, melting temperature width blended with HDPE got wider because the composition distribution at high temperature got wider. Then the relationship between stretchable temperature width and melting temperature width was investigated. As shown in **Fig.3**, three points are associated, but two points are above the line. They are the samples blended with LDPE. So this graph expresses that stretchable temperature width does not depend on only composition distribution. Therefore multiple regression analysis was used to find out factors influenced stretchability. As a result, it was found that relaxation time and molecular weight distribution in addition to the composition distribution affected stretchable temperature width.

3.3.3 The result of observation of the higher order structure

As shown in **Fig.4**, clover-shaped scattering pattern can be confirmed. So it is shown that spherulites exist. It is found that the spherulite is collapsing as the stretching proceeds. Besides as shown in **Table 4**, the sizes of spherulites of LL① and LL② are very large, but the sizes of spherulites of the samples blended with HDPE and LDPE are small. This reason is considered that HDPE and LDPE act as a nucleating agent. It can be said that a stretchable temperature width gets wider as the size of spherulite gets smaller. As shown in **Fig.5** and **Fig.6**, the scattering peak of LL① and LL② move to small-angle as temperature rises. However, the difference of them is the scattering at 130 °C. The higher order structure of LL① is not scattering to overlap BG, but the higher order structure of LL①+HD is scattering at 130 °C. In other words, crystalline phases of LL① are melting, but crystalline phases of LL①+HD exist. So it is considered that to exist crystalline phases at high temperature is to make stretchable temperature width wider. The same result can be said in **Fig.7**. At 130°C, the degree of crystallinity of LL① is 0%, but the degree of crystallinity of LL①+HD is 13%. As shown in **Table 5**, it was found that the thicknesses of crystalline phases blended with HDPE increased. So it can be said that increasing crystalline phase makes the stretching at high temperature possible.

4. Conclusion

Blending HDPE and LDPE to LLDPE is valid to make stretchable temperature width wider. It was found that blending HDPE widened composition distribution at high temperature, and blending LDPE improved entanglement of molecular chain. From the result of observing the higher order structure, it is important to exist crystalline phases at high temperature.

References

- 1) H.Uehara, K.Sakauchi, T.Kanai and T.Yamada
Int. Polym. Process 19(2), 155-179 (2004)
- 2) H.Uehara, K.Sakauchi, T.Kanai, T.Yamada
Int. Polym. Process 19(2),163-171 (2004)
- 3) H.Uehara, K.Sakauchi, T.Kanai, T.Yamada
Int.Polym.Process 19(2),172-179(2004)
- 4) S.Tamura, I.Kuramoto, T.Kanai
Polym. Eng. Sci., 1383-1393 (2012)