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The influence of chain entanglement density on ultra-drawing behavior of ultra-high-molecular-weight polypropylene in the gel-casting method

Yukiko Ikeda [a,*], Toshihiko Ohta [b]

[a] *Matsuyama Shinonome Junior College, Kuwabara, Matsuyama, Ehime 790-8531, Japan*
[b] *Ohta Laboratory, Cross Tower 1807, Osaka Bay 552-0007, Japan*

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Abstract

The ultra-drawing behavior of ultra-high-molecular-weight polypropylene (UHMW-PP) in the gel-casting method has been investigated by using four kinds of gel-cast sheets prepared from four kinds of solutions of 1.0, 2.0, 4.0 and 6.0 wt.% of UHMW-PP. Consequently, it was found that the draw ratio during neck deformation (N.DR.) was related linearly to the inverse root of solution concentration of UHMW-PP. Since this phenomenon was similar to the relationship between the attained maximum draw ratio (λ_{max}) and the solution concentration, it was considered that N.DR. was related linearly to the inverse root of chain entanglement density. And, it was also found that λ_{max} could be defined by the maximum drawing stress (F) around yield point in the 2nd step drawing. On the other hand, no influence of solution concentration on the increasing behavior of strength and modulus with ultra-drawing was detected for the gel-cast sheet prepared from initial solution concentration of above 1 wt.%. The reason of this fact was inferred from the increase of the content of shishkebab structure in the gel-cast PE fiber from the high initial solution concentration.

Keywords: Ultra-high-molecular-weight polypropylene; Ultra-drawing; Chain entanglement density

1. Introduction

To produce the high-performance (high strength and high modulus) fiber of flexible polymer, the perfect extension of folded polymer chains and the high orientation of molecules in the direction of fiber axis are required. Some studies used typical flexible polymer, for example UHMW-polyethylene (UHMW-PE) and UHMW-polypropylene (UHMW-PP), have been well known [1–18]. In the studies used UHMW-PP, the maximum strength of 1.56 GPa and the maximum modulus of 40.4 GPa have been obtained by Matsuo et al. [16]. These values were obtained in the way that the gel-cast material prepared from the dilute solution of 0.4 g/100 ml of UHMW-PP was drawn to a draw ratio (DR) of 100, that is, the gel-casting method.

It has been known that the increasing ratios of strength and modulus with ultra-drawing depend on the initial solution concentration preparing the gel-cast material, that is, as the solution concentration is dilute, the draw ratio increases and the increasing ratios of strength and modulus decrease [15,16, 19–21]. This phenomenon could be explained by the difference of chain entanglement density of UHMW-PP constituting the gel-cast material [22]. However, the relationship between the increasing ratios of strength and modulus and the chain entanglement density was made clear imperfectly.

In the previous papers [22,23], it was reported that some differences in ultra-drawing behavior were detected between the two kinds of materials of UHMW-PE [23] and UHMW-PP [22], respectively; the Gel-like Spherulite Pressing (GSP) material and the gel-cast material prepared from 2 wt.% solution with decalin. The preparing conditions of both materials were similar except for the cooling rate of solution; about 1.5 °C $\min^{-1}$ for the GSP material and about 16.5 °C $\min^{-1}$

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[*] Corresponding author. Tel.: +81 89 931 6211; fax: +81 89 933 5559.
E-mail address: yikeda@shinonome.ac.jp (Y. Ikeda).

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for the gel-cast material in the temperature range from 120 to 60 °C [22,23]. As it was considered that the chain entanglement density of the GSP material was lower than that of the gel-cast material, the influence of chain entanglement density on the differences of ultra-drawing behavior between both materials could be explained consistently [22,23].

In this paper, to clarify the influence of chain entanglement density on the ultra-drawing behavior of UHMW-PP in the gel-casting method, the four kinds of gel-cast materials with different chain entanglement density were prepared. The solution concentrations for preparing gel-cast materials were 1, 2, 4 and 6 wt.% and these concentrations were higher than that by Peguy and Manley [15] and that by Matsuo et al. [16].

2. Experimental part

2.1. Preparation of gel-cast sheets

The 1, 2, 4 and 6 wt.% solutions were prepared by heating dispersions of the constant weight of UHMW-PP ($M_w = 1.8 \times 10^6$, $M_w/M_n = 7.65$ and isotacticity of 97%, supplied by Tokuyama Co. Ltd.) powder in a stated amount of decalin for each solution to 160 °C and holding for 30 min. Approximately 0.5 wt.% (relative to the weight of the polymer) antioxidant (BHT) was mixed in the solution to stabilize the polymer. Four kinds of gel-cast materials [3] were prepared in the way that four kinds of hot solutions were quenched by pouring each solution into a stainless steel tray surrounded by dry ice and methanol.

The gel-cast sheet was prepared by compressing the accumulated gel-cast material [3] under a pressure of 50 kgf cm^{-2} and at room temperature, and subsequently drying the decalin contained in the compressed material under reduced pressure and at room temperature. The obtained sheets were about 0.5 mm thick and contained decalin of 3–5 wt.%. The sheets prepared from 1, 2, 4 and 6 wt.% solutions were called C1, C2, C4 and C6, respectively.

2.2. Preparation of drawn tape

The hot-drawing of sheet was carried out by using a tensile tester equipped with an air oven. First, the gel-cast sheet, 20 mm length and 10 mm width, was drawn to a DR of 10 at a drawing speed of 50%/min and at 130 °C. Subsequently, the predrawn tape with a DR of 10 was cut into strips, and the strips were 2nd step drawn to an appointed DR under the similar drawing conditions described above except changing the drawing temperature to 150 °C. The drawing of gel-cast sheet and predrawn tape was carried out after preliminary heating for 10 min at the above drawing temperatures (130 and 150 °C). These drawing temperatures were adopted as temperatures close to the beginning of melting in DSC curves of gel-cast sheet and predrawn tape, respectively [18,22]. The DR was given as the denier-ratio of gel-cast sheet and drawn tape.

2.3. Measurement of strength and modulus

Measurement of tensile strength was carried out with a tensile tester at a deformation rate of 50%/min and at room temperature. Measurement of dynamic modulus [18,24] was carried out with a viscoelasticity spectrometer (Iwamoto Seisakusho, VES-F-III) under the frequency of 100 Hz and at room temperature.

2.4. X-ray diffraction experiment

X-ray diffraction pattern was recorded on imaging plate. The recorded pattern was displayed on a PC screen for taking a photograph and processed on-screen, and the changes of crystalline orientation and crystalline size in the gel-cast sheet and drawn tape with ultra-drawing were measured.

As a measure of the degree of *c*-axis orientation with respect to the draw direction, the widths at half peak value of intensity profiles along the Debye–Scherrer ring of (110) diffraction in the range of ±0.2° from the center of point-like (110) diffraction, including the instrumental width, were observed [22].

As a measure of the lateral growth of crystallites for the draw direction, the integral breadths of equatorial intensity profiles of (110) diffractions, including the instrumental width, were observed [22]. The amorphous halo in gel-cast sheet and drawn tape was removed according to the method proposed by Takahara et al. [25].

3. Results and discussion

3.1. Fine structure of gel-cast sheet

WAXD patterns of gel-cast sheets of C2 and C6 are shown in Fig. 1, in which the compressed surface was parallel to the horizontal axis in the edge pattern. WAXD patterns of gel-cast sheet of C1 showed nearly the same as those of C2, and those of C4 showed nearly the same as those of C6.

The through patterns of gel-cast sheets of C1 and C2 showed the diffraction rings from the (110), (040), (130) and (111) planes. The edge patterns of those showed preferential orientation of the (040) and (130) planes to the thickness direction of sheet. From these, it was found that the gel-cast sheets of C1 and C2 were the α-form crystal of polypropylene, and that the surface of lamella oriented parallel to the surface of sheet and rotated uniformly around *c*-axis.

The through and edge patterns of gel-cast sheets of C4 and C6 showed very broad diffraction rings of $2\theta = 15.3°$ and 21.3°, and it was found that the gel-cast sheets of those were the β-form crystal of polypropylene [25,26]. It was inferred that the formation of β-form crystal in C4 and C6 sheets was due to the crystallization by gel-casting from the solution with higher chain entanglement density than that of C1 and C2. It was confirmed by X-ray diffraction experiment that the β-form crystal of C4 and C6 was converted into the α-form crystal during preliminary heating at 130 °C, which was the drawing temperature in the 1st step drawing.

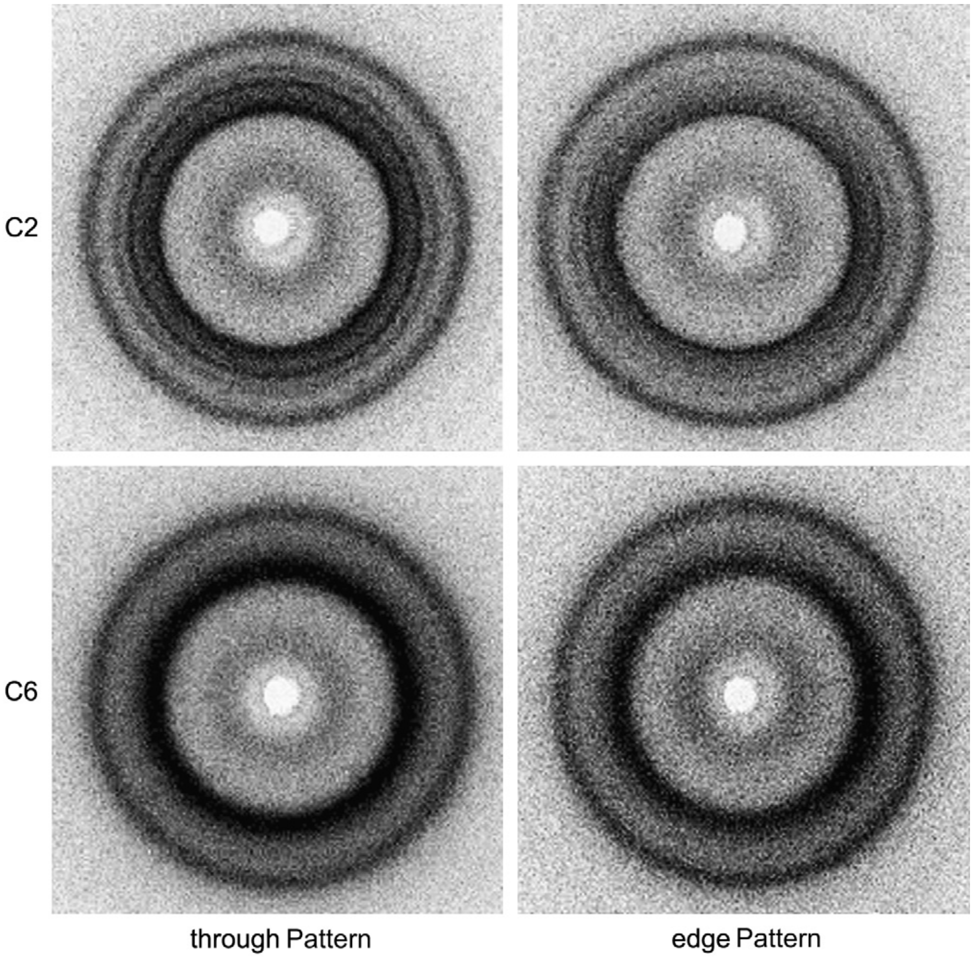

Fig. 1. WAXD patterns of gel-cast sheets of C2 and C6.

3.2. Ultra-drawing behavior

The typical neck deformation was observed in the 1st step drawing of the four kinds of gel-cast sheets at 130 °C. The maximum N.DR. was 7.6 of C1, and therefore, all sheets of C1–C6 were drawn to a DR of 10 in the 1st step drawing. Subsequently, the predrawn tape with a DR of 10 was 2nd step drawn at 150 °C, and the attained maximum draw ratio ($\lambda_{\max}$) through the 1st and 2nd step drawing was measured. Consequently, the maximum value of $\lambda_{\max}$ was 45 of C1 in this paper. For UHMW-PP in the gel-casting method, this value was lower than those reported by Peguy and Manley and by Matsuo et al.; 58 [15] and 100 [16]. However, it was considered that this value was appropriate by the reason of the fairly low molecular weight of polymer of $M_w = 1.8 \times 10^6$ and the fairly high solution concentration of 1–6 wt.%. By the way, the molecular weight was 3.4×10^6 and 4.4×10^6, and the solution concentrations were 0.75 and 0.4 wt.%, respectively, for Peguy and Manley [15] and Matsuo et al. [16].

The relationship between N.DR. and the initial solution concentration (C) is shown in Fig. 2, where N.DR. was the DR of the most drawn part in drawn tape at a DR of 3.9 on the stress–strain curve. And, the relationship between $\lambda_{\max}$ and C is shown in Fig. 3.

As shown in Figs. 2 and 3, it was found that N.DR. and $\lambda_{\max}$ were linearly related to $C^{(-1/2)}$ of C1–C6. In the investigations of UHMW-PE in the gel-casting method, it was reported that since the relationships of N.DR. $\propto C^{(-1/2)}$ [27] and $\lambda_{\max} \propto C^{(-1/2)}$ [27,28] were established, N.DR. and $\lambda_{\max}$

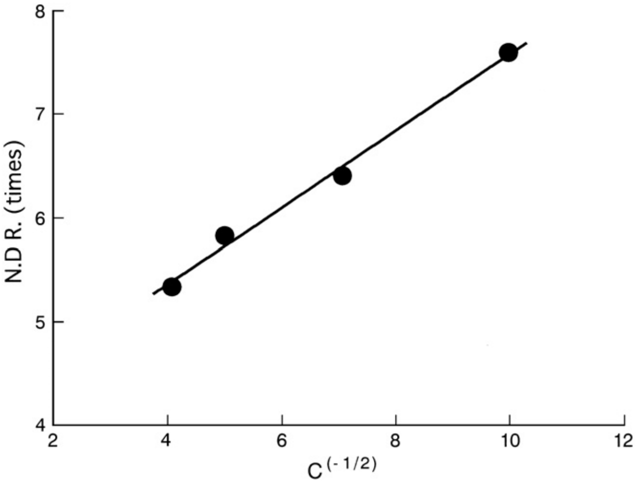

Fig. 2. Relationship between the draw ratio during neck deformation (N.DR.) and the initial solution concentration (C).

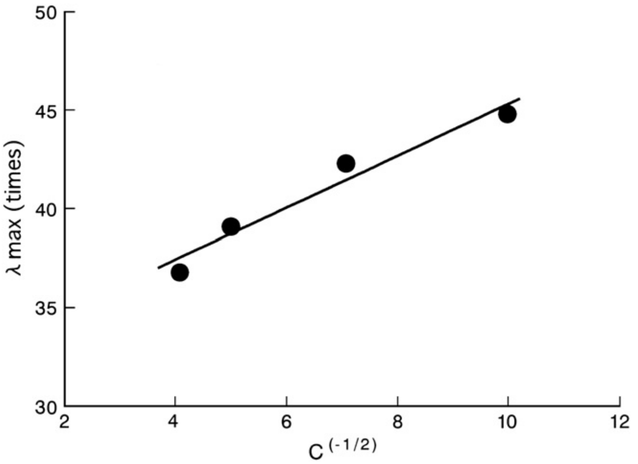

Fig. 3. Relationship between the attained maximum draw ratio (λ_{max}) and the initial solution concentration (C).

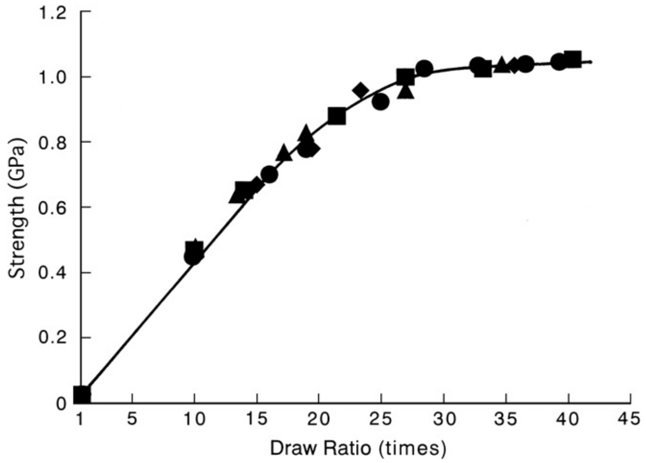

Fig. 5. Increase in strength with ultra-drawing for C1 (■), C2 (●), C4 (▲) and C6 (◆).

were proportional to the inverse root of chain entanglement density. So, also for the gel-cast sheets of UHMW-PP in this paper, it was considered that N.DR. and λ_{max} were proportional to the inverse root of chain entanglement density.

In the previous paper [24], it was suggested that λ_{max} of UHMW-PE could be predicted from the maximum drawing stress (F) around yield point in the 2nd step drawing of predrawn tape in the equation;

$$\lambda_{max} = kF^{(-1/2)}$$

So, the relationship between λ_{max} and F was observed. The result is shown in Fig. 4. It was found that a linear relationship through the origin was established between λ_{max} and $F^{(-1/2)}$ of the four kinds of gel-cast sheets of C1–C6. Furthermore, the linear slope in Fig. 4 well agreed with that of the similar investigation using GSP sheets of UHMW-PP prepared from 1, 2, 4 and 6 wt.% solutions [18]. The similar phenomenon, which is that the linear slopes well agree between the gel-casting method and the GSP method, was observed for UHMW-PE [24]. From this, it was inferred that F implied the chain entanglement density in each undrawn sheet. That is to say, it was suggested that F was enlarged for the drawn tape with high chain entanglement density and that λ_{max} was proportional to $F^{(-1/2)}$.

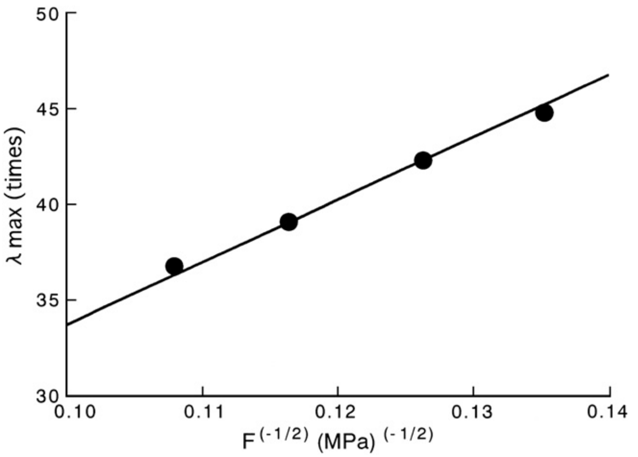

Fig. 4. Relationship between the attained maximum draw ratio (λ_{max}) and the maximum drawing stress (F) around yield point in the 2nd step drawing.

3.3. Increases in strength and modulus with ultra-drawing

The increases in strength and modulus as a result of ultra-drawing were investigated by the 2nd step drawing of predrawn tapes with a DR of 10 at 150 °C. The results are shown in Figs. 5 and 6.

Although the chain entanglement density was different among sheets, no differences of the increases in strength and modulus with ultra-drawing could be regarded as significant for C1, C2, C4 and C6. The maximum strength of 1.06 GPa of C1 at a DR = 40 and the maximum modulus of 26.6 GPa of C6 at a DR = 34 were obtained in this paper. Both values were considerably lower than both maximum values of

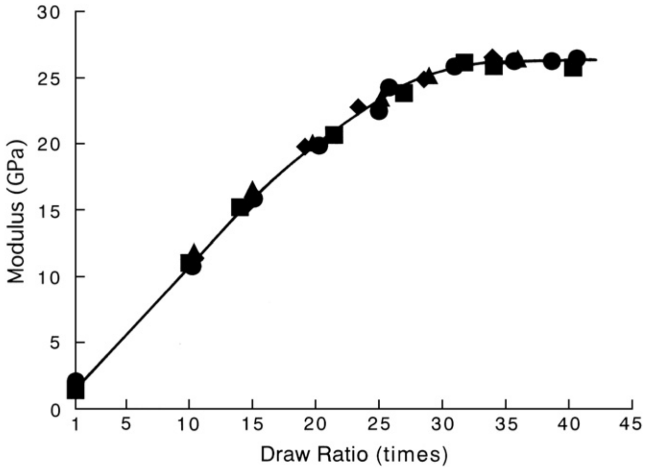

Fig. 6. Increase in modulus with ultra-drawing for C1 (■), C2 (●), C4 (▲) and C6 (◆).

1.56 and 40.4 GPa in UHMW-PP ($M_v = 4.4 \times 10^6$, at a DR = 100) reported by Matsuo et al. [16]. Comparing with the results of increases in strength and modulus in the GSP method in the previous paper [18], the increasing ratios of strength and modulus in early drawing period were higher in the gel-casting method. However, the decline of slope and the plateau of the increasing curves of strength and modulus with ultra-drawing were observed in the both method, especially those occurred at earlier period in the gel-casting method, and finally, the attained values of strength and modulus were nearly the same in the both methods.

In the previous papers on the ultra-drawing behavior of UHMW-PP [18,22], the increasing behavior of strength and modulus was discussed in relation to a chain entanglement density of undrawn sheet, and it could be explained consistently. However, the increasing behavior of strength and modulus of gel-cast sheets prepared from the solution of above 1 wt.% in this paper could not be explained in relation to only a chain entanglement density of undrawn sheet. This reason was investigated in the following item.

3.4. Structural changes relating to crystalline orientation and crystalline size with ultra-drawing

The structural changes relating to crystalline orientation and crystalline size of drawn tape with ultra-drawing were investigated by X-ray diffraction experiment.

WAXD through pattern of C2 with a DR of 10 is shown in Fig. 7. WAXD through patterns of drawn tapes with a DR of 10 of C1–C6 were very similar. Three strong diffractions of the (110), (040) and (130) planes of α-form crystal were observed in every drawn tape for C1–C6. The high degree of crystalline orientation was observed even in the drawn tapes with a DR of 10, and this indicated that the lamellar structure composed of α-form crystal in the gel-cast sheet was destroyed and transformed into the fibrous structure composed of α-form crystal with ultra-drawing.

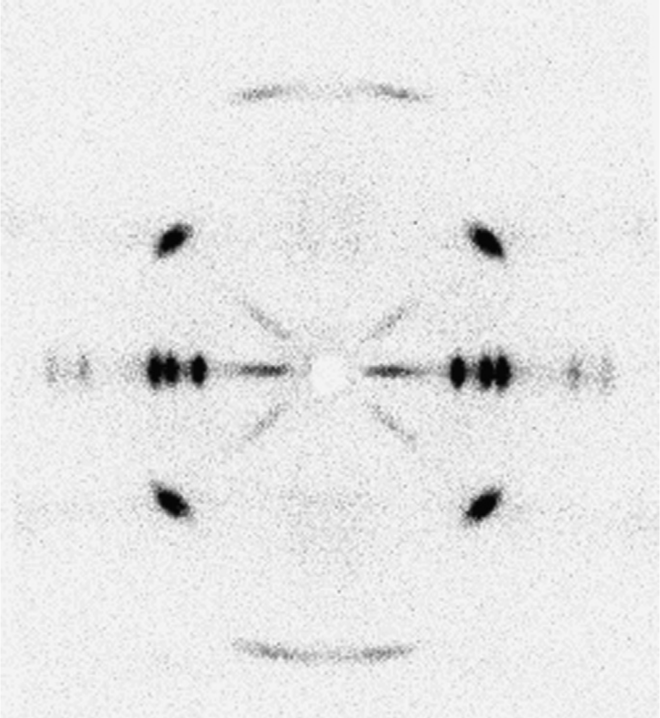

Fig. 7. WAXD through pattern of drawn tape with a DR of 10 for C2.

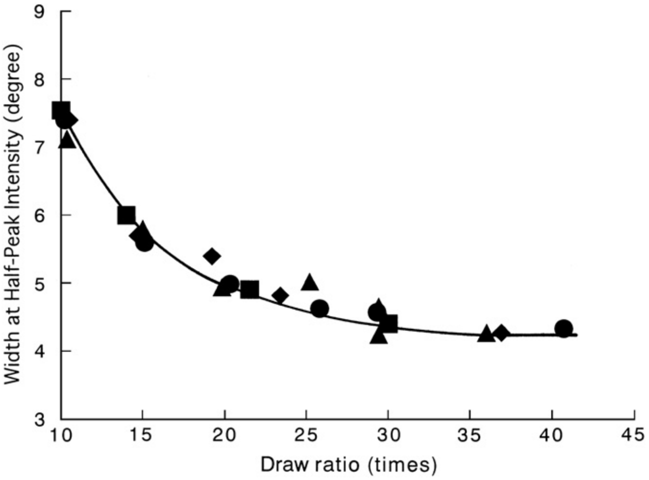

Fig. 8. Width at half peak value of intensity profile along the Debye–Scherrer ring of (110) diffraction versus DR for C1 (■), C2 (●), C4 (▲) and C6 (◆).

The changes of crystalline orientation and crystalline size with ultra-drawing at 150 °C were pursued by analyzing the intensity profiles of WAXD patterns. The widths at half peak value of intensity profiles along the Debye–Scherrer ring and the integral breadths of equatorial intensity profiles of (110) diffraction were observed to measure the degree of *c*-axis orientation and the lateral growth of crystallites for the draw direction, respectively [22]. The results are shown in Figs. 8 and 9.

Fig. 8 indicated that the *c*-axis orientation with respect to the draw direction proceeded considerably in the deformation until a DR = 20 where the linear relation of increases in strength and modulus versus DR was shown. And the change

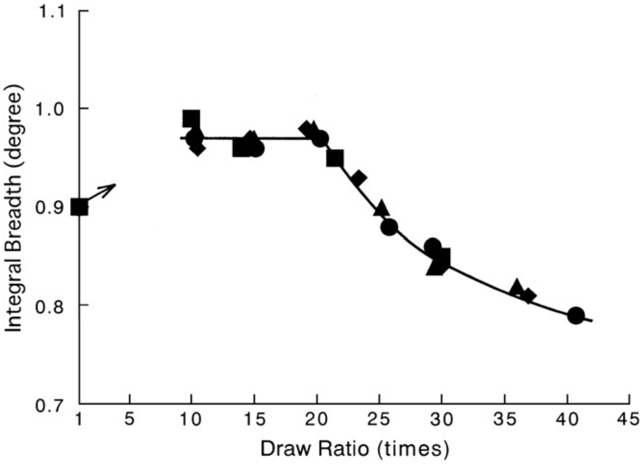

Fig. 9. Integral breadth of equatorial intensity profile of (110) diffraction versus DR for C1 (■), C2 (●), C4 (▲) and C6 (◆).

of its orientation declined in $DR \geq 20$ where the increasing ratios of strength and modulus declined, and subsequently its orientation reached to the limit beyond $DR = 33$.

Fig. 9 signified that the crystalline size changed through the three steps. In the first step, $DR \leq 10$, the stacked lamellar structure of gel-cast sheet was destroyed during neck deformation. The second step, $10 \leq DR \leq 20$, was the induction period until the increase of diameter of microfibril started [23], where microfibrils were formed during neck deformation. It was inferred that the molecular chain orientation proceeded with the constant lateral size of fibrillar crystal in this period. And, in the third step, $DR \geq 20$, the lateral growth of fibrillar crystals occurred by further drawing.

From Figs. 7–9, no differences in the structural changes relating to crystalline orientation and crystalline size with ultra-drawing of C1–C6 could be detected, although C1–C6 have some difference of chain entanglement density. Therefore, it was found that the increasing behavior of strength and modulus of C1–C6 with different chain entanglement density could not be explained from the above structural changes.

3.5. Consideration on increasing behavior of strength and modulus with ultra-drawing

It was determined from the results in the previous paper [22] that the chain entanglement density influenced on the increasing behavior of strength and modulus in these gel-cast sheets. However, no differences of the increases in strength and modulus with ultra-drawing could be regarded as significant for C1–C6 with different chain entanglement density in this paper. So, it was required to find the other structural factor which compensates for the influence of chain entanglement density on the increasing behavior of strength and modulus with ultra-drawing. Consequently, it was inferred as follow.

It was reported by Ohta et al. [29] that the presence of shishkebab structure was become clear in the gel-cast PE fiber prepared from the high initial solution concentration of 10 wt.% and the drawn fiber of the above consisted of the majority of fibrous structure with extended polymer chains and the minority of shishkebab structure which finally changed to micro-fibrous structure. From this, it was inferred for C1–C6 prepared from initial solution concentration of above 1 wt.% that as the initial solution concentration preparing the gel-cast sheet was high, the content of kebab structure in the gel-cast sheet was rich. Therefore, in the drawn tape of C1–C6 with high chain entanglement density, more kebab structure remained without destruction on them because of the difficulty of the disentanglement between molecular chains due to the high chain entanglement density, and consequently the increases in strength and modulus with ultra-drawing were depressed in these gel-cast sheets. On the other hand, in the drawn tape of C1–C6 with high chain entanglement density, the drawing stress would be more effectively transferred to each polymer chain through the chain entanglement points, and consequently the molecular orientation and fibrillar crystallization induced by chain extension were promoted more in the ultra-drawing process [22,23].

Owing to that the above two phenomena occur at the same time, the difference of the increasing behavior of strength and modulus for C1–C6 could not be regarded as significant.

4. Conclusion

Four kinds of gel-cast sheets with different chain entanglement density were prepared from four kinds of solutions of 1.0, 2.0, 4.0 and 6.0 wt.% of UHMW-PP, and the ultra-drawing behavior of those was investigated.

It was found that the draw ratio during neck deformation (N.DR.) was related linearly to the inverse root of solution concentration of UHMW-PP. Since this phenomenon was similar to the relationship between the attained maximum draw ratio (λ_{max}) and the solution concentration, it was considered that N.DR. was related linearly to the inverse root of chain entanglement density. And, it was found that λ_{max} could be defined by the maximum drawing stress (F) around yield point in the 2nd step drawing. From this, it could be suggested that the value of F was enlarged for the drawn tape with high chain entanglement density and that λ_{max} was proportional to $F^{(-1/2)}$.

On the other hand, no influence of chain entanglement density on the increasing behavior of strength and modulus was detected for the gel-cast sheet prepared from initial solution concentration of above 1 wt.%. As the other structural factor which compensates for the influence of chain entanglement density on the increasing behavior of strength and modulus, the increase of the content of shishkebab structure in the gel-cast sheet with high chain entanglement density was considered. That is to say, it was inferred that the more kebab structure remained without destruction on them due to the difficulty of disentanglement between molecular chains in the drawn tape with high chain entanglement density and that they depressed the increases in strength and modulus with ultra-drawing in the gel-cast sheet prepared from the solution of above 1 wt.%. Therefore, to clarify the effect of chain entanglement density on the increasing behavior of strength and modulus with ultra-drawing, the change of content of shishkebab structure with ultra-drawing in the drawn tape should be confirmed.

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