島根大学教育学部紀要（自然科学）第36巻　79頁～86頁　平成14年12月

Dependence of Young's Modulus of Zone-Drawing Polyethylene Fiber on the Crystallinity

Tetsuya TAKAHASHI *

高橋　哲也

ゾーン延伸ポリエチレン繊維におけるヤング率の結晶化度依存性

ABSTRACT

For the fiber produced by a continuous multi-stage zone-drawing equipment by using four different polyethylene (hereafter" PE ") samples in a range of medium high molecular weights, the relationship between fiber structure and mechanical properties was examined. The relationship between the stress of necking drawing in the first stage of continuous zone-drawing and birefringence of amorphous phase or young's modulus of the fiber obtained was linear, independent of the molecular weight. The relationship between young's modulus and the crystallinity showed a large variable dependence with a sharp rising point of the young's modulus. The crystallinity at the critical point is shifted to a higher value on increasing the drawing temperature or on decreasing the molecular weight.

These relations suggest that young's modulus influences greatly the construction of crystallite block structure and is increased by connection of crystallite blocks, which is also suggested to be related to the mobility of the molecular chain. On the other hand, the tensile strength depends mostly on the crystallinity and the molecular weight.

1. Introduction

In a plastic deformation process followed by necking of polymeric materials, crystallite block structure is constructed by the formation of microfibril structure and contributes greatly to the mechanical properties. In a hope to establish ultimate structure and ultimate properties by utilizing anisotropy of the polymer chain, a fibrous crystal growth method[1)], a gel-drawing method[2)-4)], a super-drawing method of single crystal mats[5)] and others have been proposed mostly for crystalline polymers[6)-9)]. However most examples reported for several polymers employ the material having ultra high molecular weight[1)-5)].

The author have already reported that PE fiber attaining to a dynamic young's modulus of 74 GPa could be produced continuously from PE of medium high molecular weights by a continuous zone-drawing method[10)-12)]. It was demonstrated that it attained to 80 GPa by employing a multi-step continuous zone-drawing.

In this study, four different PE's having medium high molecular weights were employed. The mechanism of crystallite block formation in the zone-drawing process and mechanical properties of the fiber obtained were examined in view of the dependence of the crystallinity.

2. Experimental

2.1 Samples

High density PE having four different molecular weights, a product of JAPAN POLYOLEFINS Co., Ltd. was

*Department of Home Economics Education, Faculty of Education, Shimane University, Matsue, Japan

melt spun by an extruder and used as an as-spun fiber. The molecular characteristics of the samples were shown in Table l. All of the as-spun fibers have a radius of 0.7-0.8 mm and a birefringence of 2.0-4.0$\times$10^{-3} without orientation.

Table. 1 Molecular characteristics of polypropylene samples.

Sample No.	Mw ($\times 10^4$)	Mw/Mn	Dens. (g/cm^3)
①	7.5	3~4	0.958
②	11.4	3~4	0.953
③	15.0	3~4	0.953
④	40.0	5~6	0.931

2.2 Drawing Process

The continuous multi-stage zone-drawing equipment employed in the experiment was shown in Fig. l. This equipment is composed of feed and take-up-rolls. The as-spun fiber extruded by the feed roll is passed through a heating band of 2 mm width equipped between rolls and subjected continuously to a smooth necking drawing. Furthermore, three heating bands of 2 mm width were installed after the 1st step necking drawing to make a three-stage non-necking drawing. Between necking and non-necking drawings, a nip roll of a drive-type was installed in order to cut off the stress.

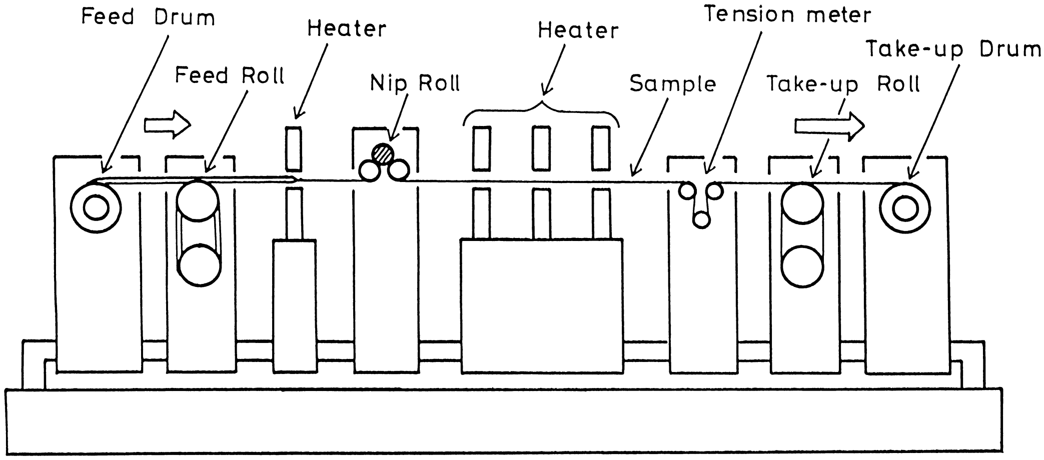

Fig. 1 Schematic representation of continuous multi-stage zone-drawing equipment

For samples 1-4, the take-up rate was changed, under the condition of drawing temperature of 95-135°C and a feed rate of 2-20 mm/min, to make fibers of 4 different drawing ratios by one-stage drawing. In order to obtain further a higher draw ratios, a three-stage non-necking drawing was undertaken after a necking drawing to make multi-stage drawn samples. For the sample 4, the drawing was impossible unless the drawing temperature was higher than 125°C and the experiment was under taken at a drawing temperature in a range of 125-150°C. The drawing stress was monitored continuously by installing a stress meter immediately before the take-up roll.

2.2 Measurements

a) Density

A density gradient tube of a water-methanol system was used. The density was measured after standing at 20°C for one day. The volume fraction degree of crystallization was calculated by using 1.00 and 0.852 g/cm^3 for densities of crystallite and amorphous phases, respectively.

b) Birefringence

The birefringence (Δn) of samples was measured by using a polarizing microscope equipped with a Na-D line light source (wavelength of 589 μm) and a Berec compensator. The birefringence of amorphous chain was calculated by using following equations:

$$\Delta n = \Delta n_c \cdot X_c + \Delta n_a \cdot (1 - X_c) \quad \cdots\cdots\cdot (1)$$

$$\Delta n_c = \Delta n_c^* \cdot f_c \quad \cdots\cdots\cdot (2)$$

Where Δn_c and Δn_z denote birefringences of crystalline and amorphous phases, irespectively. And Δn_c^* denotes an ultimate birefringence of crystalline phase, being 0.057[13] while fc means a crystalline orientation factor and Xc a volume fraction crystallinity. The morphological birefringence Δn_{form} was generally very small and neglected.

c) Wide-Angle X-ray Diffraction

X-ray generator, a product of Rigaku Co. Ltd. was used with a Cu-Kα line and a Ni-filter. The diffraction intensity curve at an output of 40 kV and 150 mA was measured by using a scintillation counter. The orientation factor along the c-axis of the crystal was obtained by the angle dependence of X-ray diffraction intensity at the (200) reflection.

d) Mechanical Properties

Dynamic modulus (E') was measured by a BIBRON DDV-II type, a product of ORIENTECH Co., was used at a driving frequency of 110 Hz, with a temperature increase rate of 2°C/min in a range of -150°C to 120°C. The tensile strength was obtained by a stress at break by using a TENSILON UTM-III-500 type of ORIENTECH Co. in a room thermostated at 23°C using a sample of 50 mm in length and a strain rate of 100%/min.

3. Results and discussion

3.1 Orientation Behavior of Amorphous Molecular Chain

The relationship between the crystallinity and the drawing stress for the zone-necking drawn fiber at the first stage at a drawing temperature of 120°C and 135°C was shown in Fig. 2(a) and (b), respectively. The molecular weight dependence was observable, the crystallinity being decreased on increasing the molecular weight. The crystallinity was increased on increasing the drawing temperature. Since the sample of 4×10^5 in the molecular weight has long-chain branches, the crystallinity appeared extremely low.

For fibers of draw ratio of more than 10, prepared by a continuous zone-drawing, the crystalline orientation

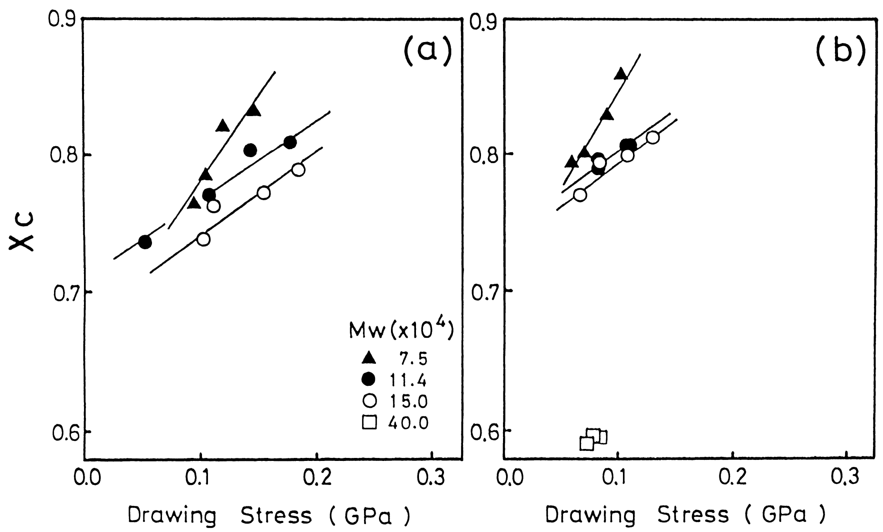

Fig. 2 Crystallinity versus drawing stress for different molecular weight : (a) drawing temperature of 120°C; (b) drawing temperature of 135°C

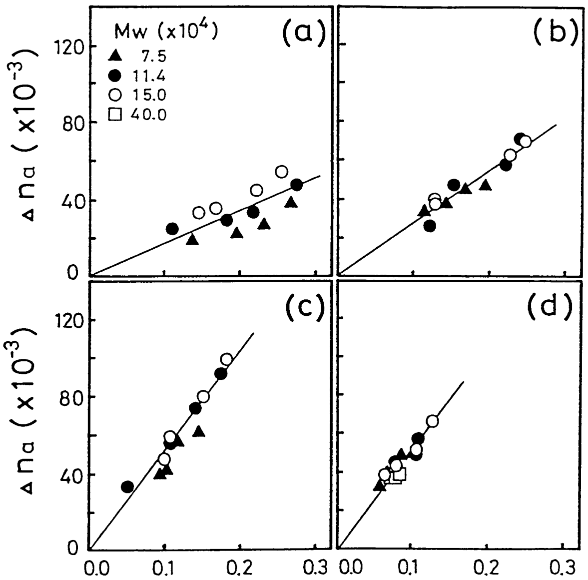

Fig. 3 Amorphous birefringence versus drawing stress for different molecular weight : (a) drawing temperature of 95°C; (b) drawing temperature of 105°C (C) drawing temperature of 120°C; (d) drawing temperature of 135°C.

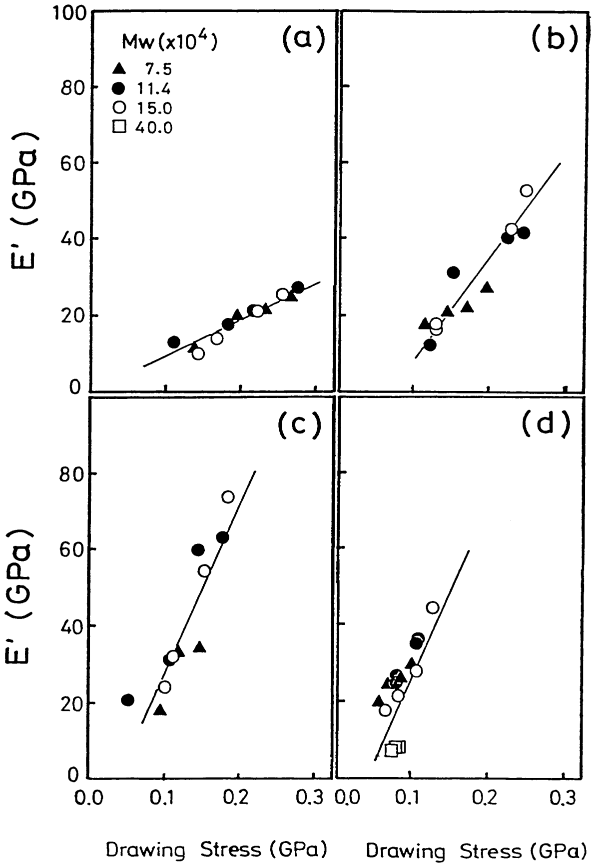

Fig. 4 Young's modulus versus drawing stress for different molecular weight : (a) drawing temperature of 95°C; (b) drawing temperature of 105°C; (c) drawing temperature of 120°C; (d) drawing temperature of 135°C

factor is assumed to be almost perfect. Therefore the birefringence of the amorphous phase was estimated from the observed birefringence minus a contribution from the crystal phase (almost constant as 0.057). In a similar way to the crystallinity, the relationship between the amorphous birefringence and the drawing stress for the necking drawn fiber at the first stage was shown in Fig. 3. No molecular weight dependence was observable and the birefringence of amorphous phase gave a straight line against the drawing stress. At a lower drawing temperature as 95°C and 105°C, independent linear relationships were obtained. However at a drawing temperature higher than 120°C, it gave a straight line, independent of the drawing temperature.

3.2 Drawing Stress and Mechanical Properties

The dependence of young's modulus on the drawing stress in a range of the drawing temperature of 95-135°C was shown in Fig. 4. Similarly to the dependence of amorphous birefringence on the drawing stress, shown in Fig. 3, it showed no molecular weight dependence and gave a straight line in a similar way to a drawing temperature dependence. For the sample having a drawing stress of 0.185 GPa at a drawing temperature of 120°C, the young's modulus attained to 74 GPa in the first stage drawing. The high modulus fiber seems to be prepared under the condition that it is drawn so as to generate a high drawing stress at a temperature higher than 120°C.

The relationship between the tensile strength and young's modulus was shown in Fig. 5 for the sample drawn at a temperature of 135°C. For any molecular weight samples, the relationship between $\log\sigma$ and logE was expressed by almost a straight line. However a molecular weight dependence was observable and a higher tensile strength appeared for the sample of higher molecular weights at the same young's modulus.

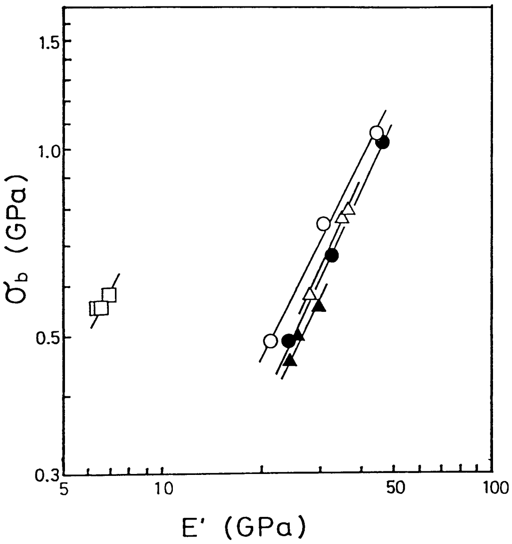

Fig. 5 Relationship between young's modulus and tensile strength for different molecular weight at drawing temperature of 135°C

3.3 Fiber Structure of Zone-Drawing Fiber

For the fiber structure generated by zone-drawing, authors have already proposed a model where the crystallite blocks are connected to each other and surrounded by oriented amorphous phase[8)10)]. The reason that the orientation of amorphous phase shows a high and stable value even at a room temperature considerably higher than the glass transition point comes from the continuous character of the crystallite block. According to the development of the continuity of crystallite blocks, the orientation factor of the amorphous phase seems to be increased. In other words, the increase of the orientation factor of the amorphous phase means the continuity of highly developed crystallite blocks. Such a filament structure seems to make an increase of the young's modulus and the tensile strength. Therefore, the dependence of amorphous birefringence, which seems to be related to the continuity of the crystallite blocks, on the crystallinity was shown in Fig. 6.

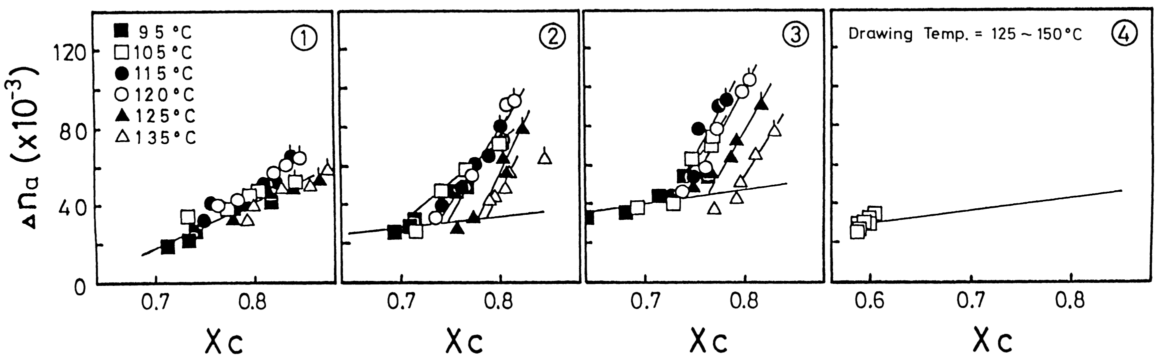

Fig. 6 Amorphous birefringence versus crystallinity for different drawing temperature : ①molecular weight of 7.5×10^4; ②molecular weight of 11.4×10^4; ③molecular weight of 15.0×10^4; ④molecular weight of 40.0×10^4;

Samples 1 to 3 were prepared at a drawing temperature of 95-135°C and a sample 4 in a range of 125-150°C. The dependence of amorphous birefringence of these fibers on the crystallinity was studied. Although data are scattered considerably for samples 2 and 3, the relationship was expressed by two linear relations. One was independent of the drawing temperature, and the other was dependent on the drawing temperature, giving a large dependence after a certain crystallinity. The value of amorphous birefringence on the latter line attained to 0.01, an extremely large value. The bar on the mark means a multi-stage drawn sample where a three step non-necking drawing was tried after a necking drawing. These locate on the extended position of each line of the drawing temperature.

Similarly, the dependence of young's modulus on the crystallinity was shown in Fig. 7. The dependence of young's modulus on the crystallinity is expressed by two linear relations, where one line is independent of the

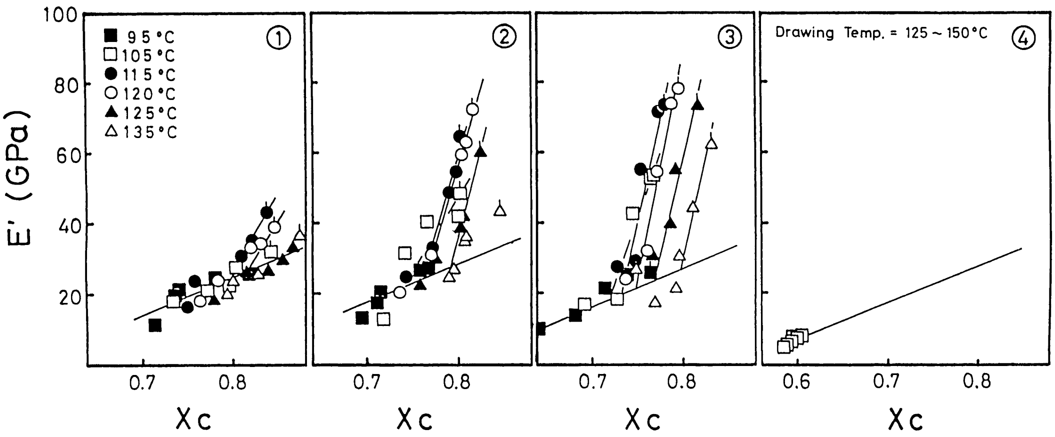

Fig. 7 Young's modulus versus crystallinity for different drawing temperature : ①molecular weight of 7.5×10^4; ②molecular weight of 11.4×10^4; ③molecular weight of 15.0×10^4; ④molecular weight of 40.0×10^4;

drawing temperature and the other becomes abruptly large after a certain crystallinity. The reason of such an abrupt change of the dependence may be related to the increase of the crystallinity followed by drawing and the continuity of the crystallite block. In other words, the probability that crystallite blocks are connected one another seems to be increased and therefore the young's modulus is increased remarkably after a certain crystallinity. At a drawing temperature of 120°C, the young's modulus of the multi-stage drawing fiber attained to 80 GPa. The samples 1-3 drawn at 95°C and the sample 4 did not show a sharp rise of the young's modulus in a range of this experiment.

The crystallinity at the critical point, where the dependence changed, was plotted against the drawing temperature in Fig. 8. The crystallinity where the dependence changed appeared at a higher value when the molecular weight was decreased. The connection of crystallite blocks may be considered to be related to the mobility of the molecular chain.

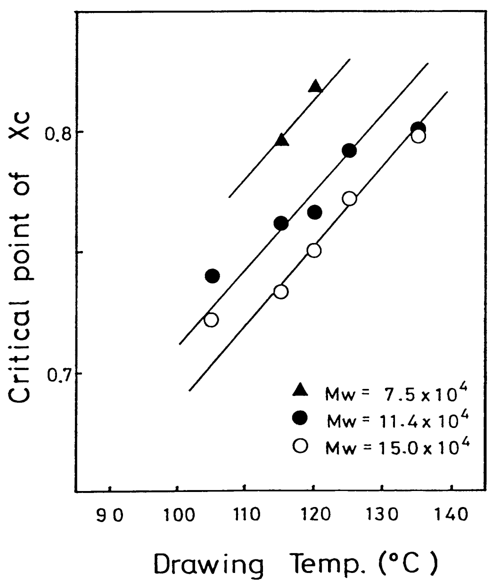

Fig. 8 Relationship between drawing temperature and the critical point of crystallinity for different molecular weight.

At this point, we will consider the model of fiber structure developed by drawing (Fig.9). (B) and (C) show the sample where Young's modulus increased abruptly after the rising point in a continuous zone-drawing and the one before the critical point, respectively. (A) is a sample of a super drawn single crystal of PE having a ultra high molecular weight. Since, in (A) the heat contraction did not start near the melting point, a monophasic structure model where defects such as molecular chain ends are distributed randomly is acceptable.

On the contrary, for the sample where high mechanical properties were obtained by a continuous zone-drawing of PE having medium high molecular weights, the heat contraction did not occur until the crystal scattering temperature and high young's modulus were observable. Once the crystallite block is destroyed, a sharp heat contraction occurred and both the amorphous orientation and young's modulus were decreased remarkably. Therefore a model of continuous crystallite blocks such as (B) is conceivable.

The dependence of tensile strength on the crystallinity was studied, too. Although the data are scattered considerably, the tensile strength depended on the increase of the crystallinity. When molecular weight increased, it appeared at a higher value on the same crystallinity.

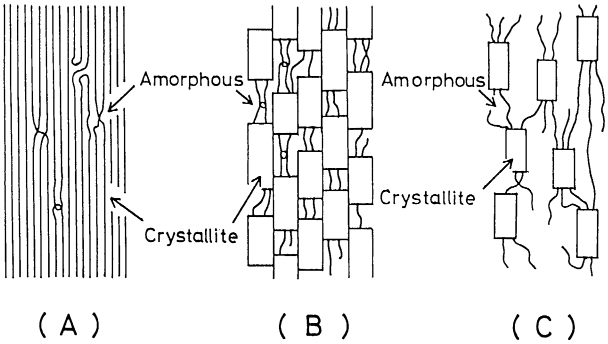

Fig. 9 Schematic representation of fiber structure : (A) continuous crystallite model ; (B) intercrystallite bridge model ; (C) conventinal crystallite model.

On the other hand, the dependence of tensile strength on the crystallization was shown in Fig. 10. Although the data are scattered considerably, the tensile strength depended on the increase of the crystallization. When molecular weight increased, it appeared at a higher value on the same crystallization.

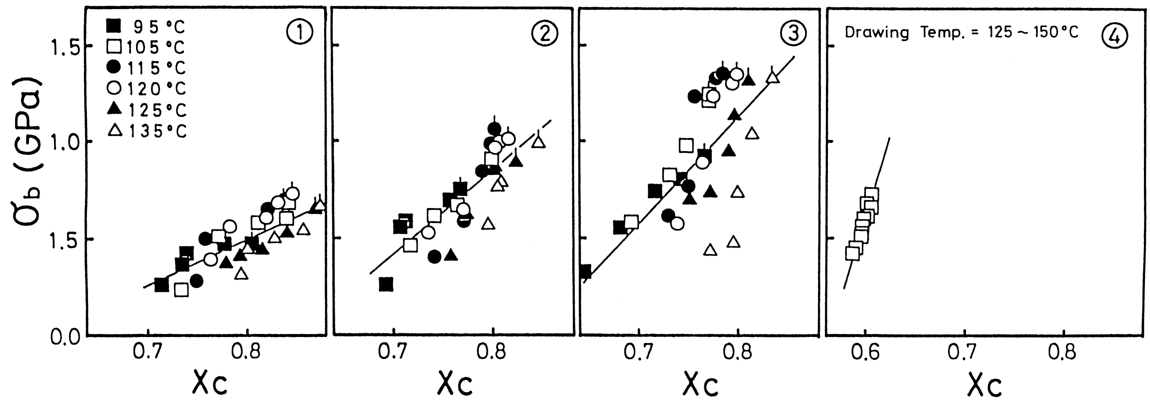

Fig. 10 Tensile strength versus crystallinity for different drawing temperature : ①molecular weight of 7.5×10^4; ②molecular weight of 11.4×10^4; ③molecular weight of 15.0×10^4; ④molecular weight of 40.0×10^4;

4. Conclusions

The relation between fiber structure and mechanical properties of the fiber prepared by a continuous zone-drawing equipment from four different PE samples having medium high molecular weights were examined.

(1)Young's modulus did not depend on the molecular weight and were related directly to the drawing stress. At a drawing temperature higher than 120°C, it was expressed by a single linear relation, irrespective of the drawing condition.

(2)The birefringence of amorphous phase did not depend on the molecular weight and showed an excellent linear relation with a drawing stress. At a drawing temperature higher than 120°C, it was expressed by a single linear relation.

(3)The dependence of birefringence of amorphous phase on the crystallinity for the samples of molecular weights of 1.14×10^5 and 1.50×10^5 was expressed by two linear relations. At a certain crystallinity dependence was changed to increase sharply. The birefringence of amorphous phase attained to 0.10.

(4)The dependence of young's modulus on the crystallinity was expressed by two linear lines. It changed at a certain crystallinity and Young's modulus increased remarkably after this point. The reason was assumed as that the fiber structure, where the crystallite blocks were connected to one another, was generated after this range of crystallinity. The critical point, where the dependence changed remarkably, was shifted to a higher value when the drawing temperature was increased or the molecular weight was decreased. Therefore the connection of the crystallite blocks may be related to the mobility of the molecular chain.

(5)The multi-stage drawn samples, where a three-stage non necking drawing was applied after a necking drawing, were fitted on the extended line obtained for the non-stage drawing sample. The young's modulus of the multi-stage drawn fiber at a temperature of 120°C attained to 80 GPa.

(6)The tensile strength depended mostly on the crystallinity and appeared a higher value on increasing the molecular weight.

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