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The ultra-drawing behaviour of ultra-high-molecular-weight polypropylene in the gel-like spherulite press method: influence of solution concentration

Toshihiko Ohta[a,*], Yukiko Ikeda[a,], Michiyo Kishimoto[a], Yuriko Sakamoto[a], Hidetoshi Kawamura[b] and Eitaro Asaeda[b]**
[a]*Faculty of Human Life Science, Osaka City University, Sumiyoshi, Osaka 558, Japan*
[b]*Plastic Research Laboratory, Tokuyama Corp., Harumi-cho, Tokuyama City, Yamaguchi 745, Japan*

The influence of solution concentration on ultra-drawing in the gel-like spherulite press (GSP) method has been investigated using four kinds of gel-like spherulite formed from 1.0, 2.0, 4.0 and 6.0% w/w solutions of ultra-high-molecular-weight polypropylene (UHMW-PP). The ultra-drawing behaviour and the increase of strength and modulus are discussed with respect to the effect of chain entanglement density. It was concluded that ultra-drawing in the GSP-method was progressed by the deformation of three-dimensional networks formed by chain entanglements, though there were no (or fewer) connections between the initial gel-like spherulites used as a starting material. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

In ultra-high-molecular-weight polyethylene (UHMW-PE) there had been good progress in the processing methods for obtaining high performance materials after development of the gel-spinning method[1], i.e., the gel-like spherulite press (GSP) method[2], single crystal drawing[3,4], virgin-polymer-film drawing[5] and reactor-powder drawing[6]. All of these methods are characterized by the use of separated particles, and hence, the process of pressing them is required for ultra-drawing in these methods.

The GSP-method developed in 1983 by Ohta et al.[7] was effective way of producing high-performance organic materials having a large cross-sectional area such as rods and thicker tapes. This method is distinct from the other methods in that the gel-like spherulites formed from a semi-dilute solution are used; chain entanglements are introduced between lamellae in the gel-like spherulites, but there are no, or fewer, chain connections between spherulites[8]. There are no, or fewer, chain connections between lamellae in single crystal, or virgin polymer film drawing, and no spherulites in gel-spinning/casting.

In previous papers[8–10] it was shown that the ultra-drawing behaviour of UHMW-PE in the GSP-method was barely influenced by spherulite size and the lack of chain connection between the spherulites, and could be treated as the deformation of three-dimensional networks composed of chain entanglements trapped in a gel-like spherulite. So, it is interesting to elucidate the ultra-drawing behaviour of other polymers to determine the influence of the initial solution concentration in the GSP-method. Moreover, there

are some studies on the ultra-drawing of UHMW-PP using the gel-casting method[11,12] and single-crystal-extrusion method[13]. Through these studies, the maximum strength of 1.56 GPa and the maximum modulus of 40.4 GPa were shown[12], but it was not practical to prepare all the gel-casting specimens from the dilute solution (below 0.75% w/w).

In this paper, the ultra-drawing behaviour of UHMW-PP (ultra-high-molecular-weight polypropylene) in the GSP-method is investigated by use of four kinds of gel-like spherulite formed from different semi-dilute solutions.

EXPERIMENTAL

Preparation of gel-like spherulites

UHMW-PP of $M_w = 1.8 \times 10^6$ was supplied by Tokuyama Co. Ltd., which showed $M_w/M_n = 7.65$ and iso-tacticity of 97% expressed by m m m m pentad. Gel-like spherulites from this polymer were separately formed until solution concentrations were 6.0 to 6.5% w/w. This fact, different from the case of UHMW-PE[9], was favourable for elucidating the influence of initial solution concentration.

The 1, 2, 4 and 6% w/w solutions were prepared by heating dispersions of UHMW-PP powder in decalin to 160°C and holding for 30 min. Approximately 0.5% w/w (relative to the weight of the polymer) antioxidant (BHT) was mixed in the solution to stabilize the polymer. Four kinds of gel-like spherulite from 1.0, 2.0, 4.0 and 6.0% w/w solutions were prepared by cooling each solution at a rate of about 1.5° min^{-1} from 120 to 60°C.

Measurement of decalin content in a gel-like spherulite

A tiny drop of the suspension of gel-like spherulites in decalin was put on a filter paper for 1 to 3 min until the

surface of the spherulites became cloudy owing to removal of decalin existing between the spherulites. A small amount (8 to 10 mg) of such gel-like spherulites was used to measure the decalin content. The amount of decalin was deduced from the thermogravimetric curve of the cloudy specimen, obtained with a thermogravimetric analyser (Rigakudenki, TAS-100) under the following conditions: heating at a constant rate of $20°$ min^{-1} to $100°C$, holding for 10 min at this temperature, then heating again at $10°$ min^{-1} from 100 to $200°C$.

Preparation of GSP-sheet[8]

Gel-like spherulite pressing sheet (called a GSP-sheet for short) was prepared by compressing the accumulated material of the gel-like spherulites under a pressure of 50 kg cm^{-2} at room temperature for 15 min and subsequently drying the decalin contained in the compressed material under reduced pressure at room temperature. The obtained sheets contained 3 to 4% w/w decalin and showed ultra-drawability of draw ratio of 40 to 50. Each sheet was used as a specimen for ultra-drawing. The specimens prepared from 1, 2, 4, and 6% w/w solutions were called A1, A2, A4 and A6, respectively. All specimens were 0.5 mm thick.

Preparation of drawn tape

The hot-drawing of specimens was carried out using a tensile tester equipped with an air oven. First, GSP-sheets 20 mm long and 10 mm wide were drawn to a length of 200 mm (draw ratio (DR) = 10) at a drawing speed of 10 mm min^{-1} at $130°C$. Subsequently, these predrawn tapes were cut into strips 40 mm long, which were again drawn to various lengths under the above drawing conditions at $150°C$. The drawing of specimens was carried out after preliminary heating for 10 min at the above drawing temperatures ($130°C$ and $150°C$). Both drawing temperatures were adopted as temperatures close to the beginning of melting in d.s.c. curves of GSP-sheets and their predrawn tapes, respectively. During preliminary heating at $130°C$ for

GSP-sheets, a small increase of the long period from 97 Å to 106 Å was observed. This fact would not have an influence on the density of chain entanglement in GSP-sheets. The draw ratio was given as the denier-ratio of undrawn and drawn specimens.

Measurement of strength and modulus

Measurement of tensile strength was carried out at room temperature with a tensile tester under the following conditions: cross-head distance 5 cm, deformation rate 50% min^{-1}, flat plate chuck of 5 cm. In measuring the modulus of high-modulus specimens with a tensile tester, slight slippage in a chuck may cause a large observational error, especially in the case of short specimens. The agreement of dynamic and tensile modulus was confirmed in a gel-spun fibre of UHMW-PE. In this study, therefore, a dynamic modulus under the frequency of 100 Hz at room temperature was measured. A viscoelasticity spectrometer (Iwamoto Seisakusho, VES-F-III) was adopted for measuring the dynamic modulus of the specimen.

RESULTS AND DISCUSSION

Formation and properties of gel-like spherulites

Figure 1 shows polarized microscopic photographs of the gel-like spherulites prepared from 1, 2, 4 and 6% w/w solutions. All the spherulites show similar morphology, with fibril-like lamellae growing parallel to the radial direction of the spherulite. However, they differ in size: spherulites from the 1% w/w solution are 50 ± 3 μm in diameter, while those from the 2, 4, 6% w/w solutions are 65 ± 7, 80 ± 10 and 45 ± 12 μm, respectively. The volume of each spherulite formed from the 1, 2 and 4% w/w solutions, calculated from their diameters, is linearly proportional to the polymer concentration in the initial solution. Considering that the polymer concentrations in each spherulite from the solutions of 1 to 6% w/w are very close as shown in *Figure 2*, it is found that the total number of primary nuclei for a fixed volume of initial solution is almost the same for the semi-dilute solutions from
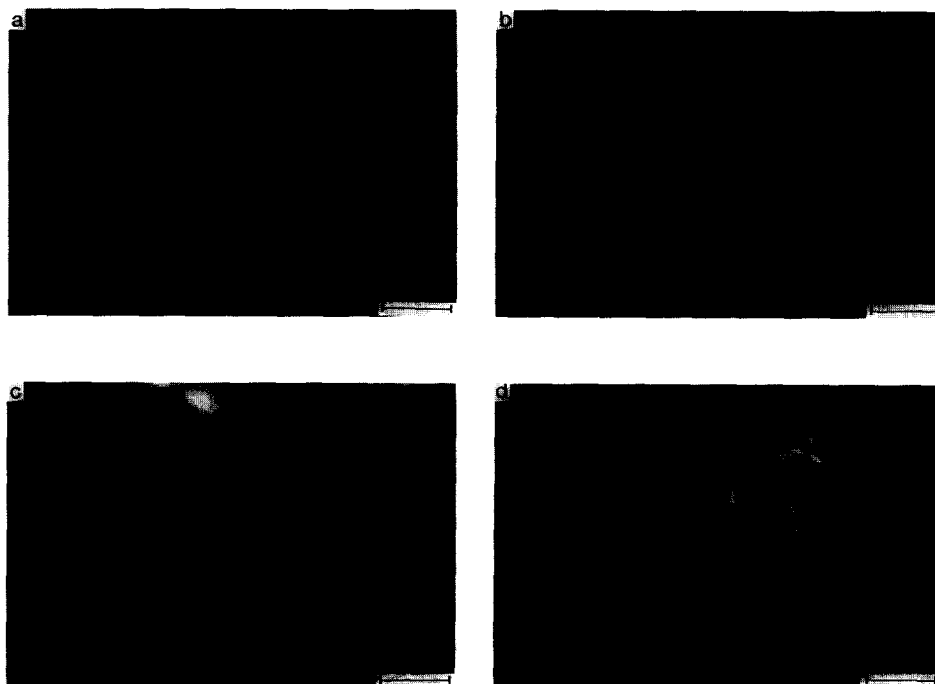

Figure 1   Polarized microscopic photographs of the gel-like spherulites prepared from (a) 1% w/w, (b)2% w/w, (c) 4% w/w and (d)6% w/w solutions (the scales on photographs are 50 μm length)

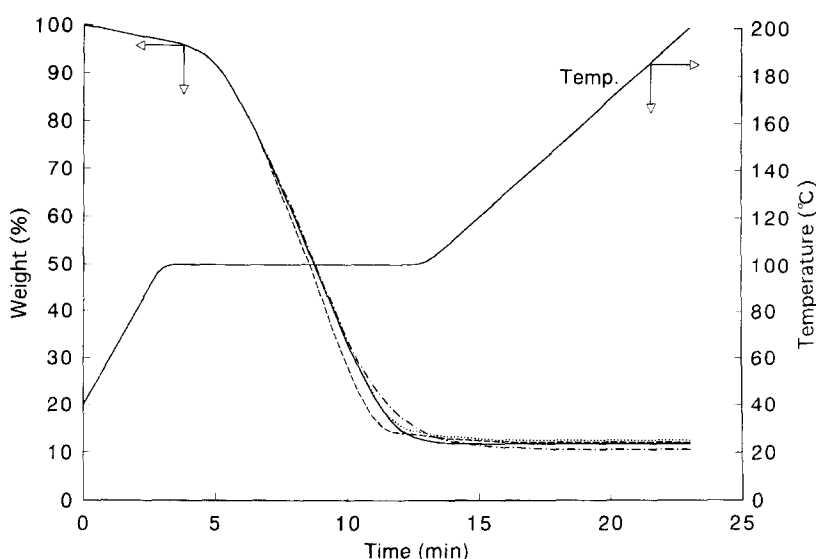**Figure 2** Thermogravimetric curves of the gel-like spherulites formed from 1% w/w (—————————), 2% w/w (——————), 4% w/w (— — —) and 6% w/w(·············) solutions

1 to 4% w/w. The size of spherulites from the solution of 6% w/w deviates from this relation, which is smaller than that from the solution of 1% w/w. This is inferred to be due to collision between spherulites in their growth process.

Individual gel-like spherulites are too small to be termed 'gel', but contain much solvent. They have the properties of a free drain gel, as they exhibit elasticity and exude solvent when they are compressed. Thermogravimetric curves of the spherulites, after removal of the decalin existing between them, are shown in *Figure 2*. Gel-like spherulites formed from 1, 2, 4 and 6% w/w solutions show the similar evaporation behaviour of decalin. The decalin contents in the gel-like spherulites formed from 1, 2, 4 and 6% w/w solutions are 88, 88, 89 and 87% w/w respectively, that is, the polymer concentrations in the gel-like spherulites are about 12% w/w, independent of the initial solution concentration. It is found from this that the difference of chain entanglement density between gel-like spherulites becomes remarkably closer than that between initial solutions of 1 to 6% w/w during formation of gel-like spherulites.

Fine structure of GSP-sheet

Four kinds of GSP-sheet A1, A2, A4 and A6 showed almost the same X-ray diffraction patterns with respect to crystalline orientation. In *Figure 3*, WAXD and SAXS patterns of a GSP-sheet from 2% w/w solution are shown as examples in which the compression surface is parallel to the horizontal axis in edge pattern. The edge pattern of WAXD

shows preferential orientation of the (040) and (130) planes of α-form crystal in the horizontal direction. This indicates that the lamellar surface is oriented parallel to the surface of GSP-sheet and is uniformly rotating around the c-axis. In the edge pattern of SAXS, strong interference from long-period structure of 97 ± 1 Å is observed in the direction of GSP-sheet's thickness, which corresponds to the lamellar thickness. This indicates that a GSP-sheet is composed of a multilayer structure formed by accumulation of lamellae and each lamella is well packed. Such a structure of the GSP-sheet would be given by reorientation of lamellae in a gel-like spherulite during compression of 15 min, as shown in a previous paper[8]. Each lamella grown in the radial direction of a spherulite reorients so that the lamellar surface is oriented parallel to the plane of compression under the torque given by a compression[8].

Ultra-drawing behaviour

Since the difference between nominal stress-strain curves at 130°C in the 1st stage of drawing of GSP-sheets A1, A2, A4 and A6 could not be detected, only that of A2 specimen was shown in *Figure 4*. Clear neck deformation was observed and the drawing stress gently increased from 0.035 to 0.048 g d^{-1} at the draw ratio (*DR*) of 10. Their *DR* after neck deformation, given by the denier ratio of undrawn part and drawn part at *DR* of nearly 3.9 on the stress–strain curves, showed a fixed value of 8.0 ± 0.5. Such good agreement must result from little difference between chain
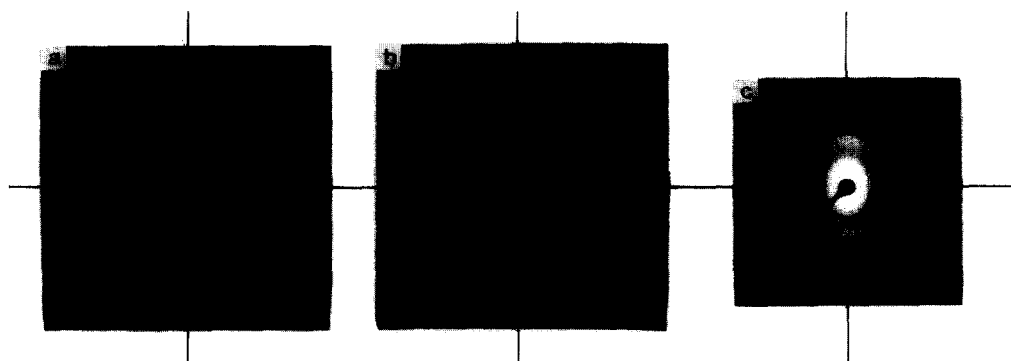

Figure 3 WAXD and SAXS patterns of the GSP-sheet from 2% w/w solution, with the surface parallel to the horizontal axis: (a) through pattern of WAXD; (b) edge pattern of WAXD; (c) edge pattern of SAXS (four diffraction rings in (a) and (b) are assigned to (110), (040), (130), and (111) planes in order of the inner side)
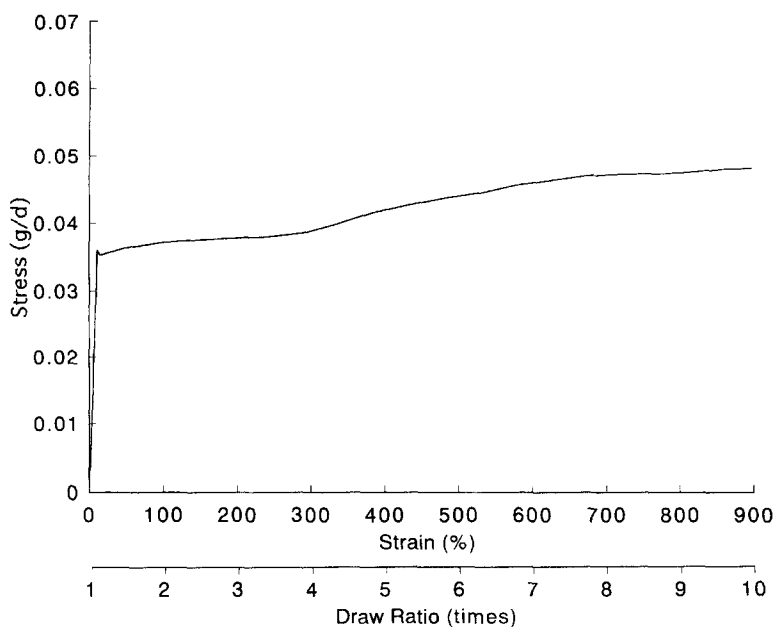
Figure 4 Nominal stress–strain curve at 130°C in the 1st stage of drawing of specimen A2

entanglement density of GSP-sheets. The decreasing ratios of thickness and width as a result of necking were 82% and 28%, respectively. The decrease of thickness is remarkably larger than that of width. This fact, considering that the GSP-sheet is composed of a stack of lamellae, is inferred to be due to the extension of folded polymer chains in neck deformation.

Nominal stress–strain curves at 150°C in the 2nd stage of drawing of predrawn tapes of $DR = 10$ are shown in *Figure 5* for specimens A1, A2, A4 and A6. The maximum draw ratios (λ_{max}) through the 1st and 2nd stages of drawing are in the region of 41 to 50. These values are much lower than those for UHMW-PE in the GSP-method[9]: 136 for A2, 143 for A1. It is considered there are many reasons for this—i.e., shorter molecular chain length in this specimen ($M_w = 1.8 \times 10^6$) than in UHMW-PE ($M_w = 2 \times 10^6$)[9], the difference of fine structure of GSP-sheet based on the difference of molecular chain conformation, and so on.

Furthermore, the difference of λ_{max} between specimens A1, A2, A4, and A6 is very small, as is that of UHMW-PE in the GSP-method[9], which is considerably smaller than that of UHMW-PE in the gel-casting method[14]. This characterizes the ultra-drawability in the GSP-method, which is considered to originate from the small difference of chain entanglement density between gel-like spherulites. Such little difference of λ_{max} between specimens seemed to be related to the yield stress (F) in the 2nd stage of drawing as shown in *Figure 5*, that is, the higher the yield stress (F), the lower is λ_{max}. The differences of λ_{max} and F between predrawn tapes with $DR = 10$ were considered to be a sensitive indication of a small increase in the difference of chain entanglement density between gel-like spherulites. This small difference, moreover, would be retained by them as a memory effect of chain entanglement density in an initial solution.

In the deformation of highly oriented materials such as the above predrawn tapes, especially, yield stress (F) and
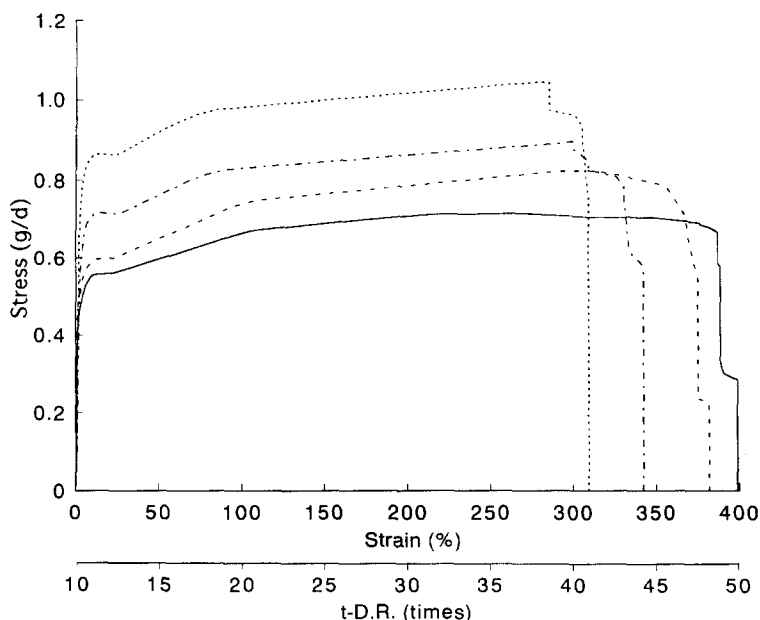

Figure 5 Nominal stress–strain curves at 150°C in the 2nd stage of drawing of predrawn tapes of $DR = 10$ for specimens A1 (——), A2 (- - -), A4 (—·—·—) and A6(············)
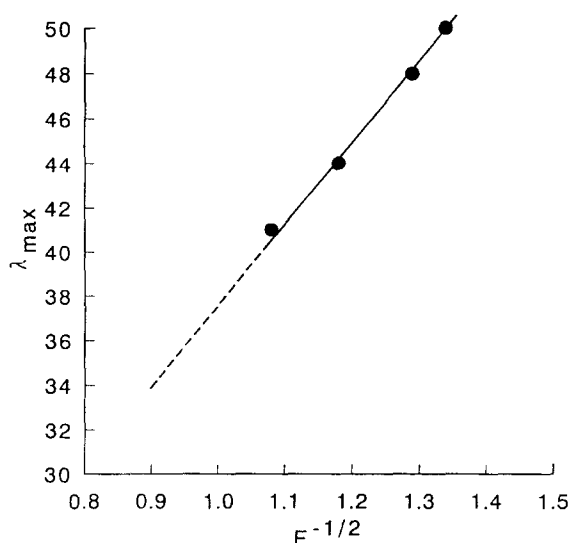
Figure 6 The relationship between the maximum draw ratio (λ_{max}) and the yield stress (F)

drawing stress in the 2nd stage of drawing are considered to be a sensitive indication of a small difference of chain entanglement density among them, because control of chain slip and transfer of tensile force into molecular chains through the chain entanglement points contribute considerably to the stress and strain in 2nd stage of drawing. In contrast, no effect of chain entanglement density on those in the 1st stage of drawing was observed as shown in *Figure 4*, the effect of which was inferred to be relatively insensitive to the deformation resulting from extension of folded polymer chains. Thereupon, the relation between λ_{max} and F was investigated, and consequently a linear relationship through the origin was established between λ_{max} and $F^{-1/2}$, as shown in *Figure 6*. The same relation had been established for GSP-sheets of UHMW-PE[9]. This result will be discussed with relation to ultra-drawing mechanism of GSP-sheet.

Increase in strength and modulus by ultra-drawing

The increase in strength and modulus as a result of ultra-drawing was investigated by 2nd stage of drawing at 150°C of predrawn tapes with $DR = 10$. The result is shown in *Figures 7 and 8*. The increases in strength and modulus as a result of ultra-drawing are almost the same for specimens
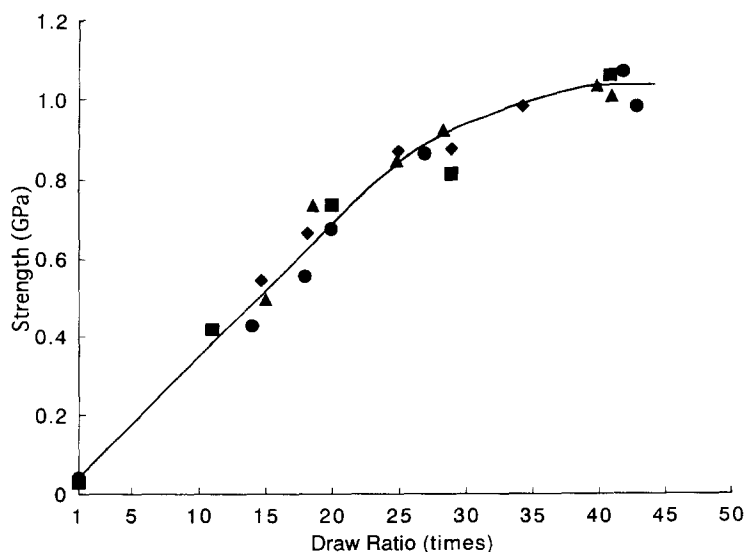
A1, A2, A4 and A6, independent of initial solution concentrations. This fact is considered to be mainly due to the small difference of chain entanglement density between each specimen. A linear relation of strength and modulus *versus DR* is observed for $DR \leq 25$. The slopes of strength and modulus *versus DR* gradually decline from $DR = 25$ as the DR increases, and exhibit a plateau at $DR \geq 41$. Consequently, the maximum strength of 1.1 GPa and the maximum modulus of 26.7 GPa are obtained. Such increasing behaviour of strength and modulus are similar in shape to those of UHMW-PE 10 in GSP-method and gel-casting method.

The above slopes of strength and modulus in $DR \leq 25$ are looser for GSP-sheet than for the gel casting sheet[15] prepared by rapid cooling of an initial solution of 2% w/w of UHMW-PP in this paper. Considering that the difference of processing conditions for both sheets from 2% w/w solution was only the rate of cooling of the solution, the difference in slope would be assigned to the difference of chain entanglement density between both specimens. Therefore, it was deduced that the chain entanglement density of GSP-sheets A1, A2, A4 and A6, showing a common slope of strength and modulus *versus DR*, decreased remarkably from those in their initial solutions of concentrations above 2% w/w. This decrease would be caused by disentanglement between polymer chains in an initial solution, during formation of gel-like spherulite from solution. Moreover, the slopes of strength and modulus in $DR \leq 25$ are in good agreement with the modulus in the gel-casting specimen from a solution of 0.75% w/w by Manley et al. [11], but steeper than those of strength and modulus in the gel-casting specimens from solutions of about 0.5% w/w by Matsuo et al.[12]. From this fact, the chain entanglement density of GSP-sheets seems to be nearly equal to that of gel-casting specimen by Manley et al.[11] and higher than that of Matsuo et al.[12], but it is difficult to discuss thus relations at present because the difference of polymer chain length (or molecular weight) is mutually too large; $M_w = 3.4 \times 10^6$ for Manley et al.[11], $M_v = 4.4 \times 10^6$ for Matsuo et al.[12].

The change of slopes of strength and modulus in $DR \geq 25$ was considered to correspond to the transition to the destruction process of the fibrillar drawn structure, by analogy with that in UHMW-PE[10]. The attained strength and modulus of 1.1 GPa and 26.7 GPa are considerably

Figure 7 The increase in strength with ultra-drawing by the second hot-drawing at 150°C of the predrawn tapes with a $DR = 10$ for specimens A1 (■), A2, (●), A4(▲) and A6 (◆)
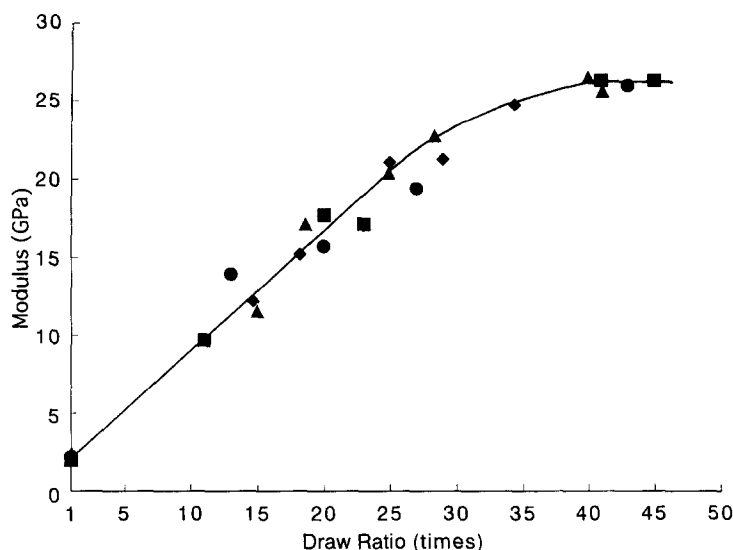
Figure 8 The increase in modulus with ultra-drawing by the second hot-drawing at 150°C of the predrawn tapes with a $DR = 10$ for specimens A1 (■), A2, (●), A4(▲) and A6 (◆)

lower than both maximum values[12] of 1.56 GPa and 40.4 GPa in UHMW-PP. However, if the 3rd stage of drawing under the appropriate conditions, such as the drawing temperatures of above 150°C, was adopted for A1, A2, A4 and A6, both properties would approach maximum values[12]; it is, however, difficult to attain these because the difference of polymer chain length[12] was too large.

Relation of strength and modulus

In the Griffith theory[16], the relationship between strength (σ) and modulus (E) is shown by the equation $\sigma = m \cdot E^{1/2}$, in which m is inversely proportional to the square root of crack size. Griffith plots of high modulus PE fibres prepared by various methods are shown in a previous paper[17]. The value of m depends largely on the processing method; 0.35 to 0.60 GPa$^{1/2}$ for gel-spinning (or casting), 0.12 to 0.24 GPa$^{1/2}$ for hot drawing of melt spun, 0.03 GPa$^{1/2}$ for solid state extrusion. This result shows that the higher the value of m, the more appropriate the processing method for obtaining high-strength fibre. Ultra-drawing in GSP-method is possible only after compressing the accumulated material of gel-like spherulites, because there are no (or fewer) connections between them. This fact suggested that cracks

(or defects) along the boundary surface between lamellae belonging to adjacent(or different) spherulites would be formed by compression of spherulites. Then, the influence of crack (or defect) formation on the increase of strength was investigated using the Griffith equation.

Griffith plots for GSP-sheets A1, A2, A4 and A6 are shown in *Figure 9*, drawn using the data from *Figures 7 and 8*. A linear relationship was observed in the region of $E \geq$ 9 GPa. This indicates that the Griffith theory is applicable to only the highly oriented state of $DR \geq$ 10 after neck deformation and the size of crack (or defect) is fixed until the destruction process is reached. The value of $m =$ 0.31 GPa$^{1/2}$ was obtained, which was somewhat lower than the range[17] of the gel-spinning (or casting) method for UHMW-PE, but in good agreement with that of gel-casting method for UHMW-PP[15]. It was concluded from this that the size of crack (or defect) formed by compression of spherulites and neck deformation of GSP-sheet was in the range of that in the gel-casting method for UHMW-PP.

Ultra-drawing mechanism in the GSP-method

As described above, λ_{max} of GSP-sheets A1, A2, A4 and A6 could be related to their yield stresses (F) in the 2nd
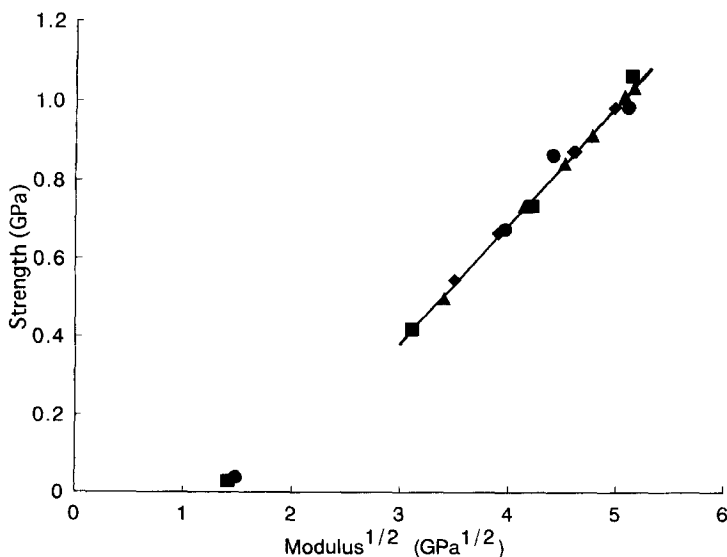

Figure 9 Griffith plots of GSP-sheets A1 (■), A2, (●), A4(▲) and A6 (◆)

stage of drawing. It was found that λ_{max} was proportional to $F^{-1/2}$. By simple assumption that F is linearly proportional to the chain entanglement density in a predrawn specimen, as described in the previous paper[9], this leads to the relationship between λ_{max} and the contour length (L) of a chain segment between crosslinking points in the elastic theory of rubber elasticity. This indicates that the ultra-drawing of GSP-sheets can be explained by the deformation of three-dimensional networks composed of chain entanglements trapped in a gel-like spherulite, despite no (or fewer) connections between gel-like spherulites used as a starting material.

Such ultra-drawing mechanism in the GSP-method can be understood by the formation of pseudo-three-dimensional networks composed of chain entanglements in the GSP-sheet. It is considered that they are easily formed in a GSP-sheet during compression of the accumulated material of gel-like spherulites including as much decalin as 88% w/w. The formation of networks in this way can be explained rationally by considering that the chain entanglements trapped in a gel-like spherulite are uniformly dispersed over the GSP-sheet by the deformation of gel-like spherulites during their compression for 15 min. More explicitly, lamellae belonging to adjacent spherulites are mixed together during compression of the accumulated material of gel-like spherulites, and then the boundary surfaces of the spherulites disappear in the multilayer lamellar structure of the GSP-sheet. This consideration was supported by the fact that the compressed sheets prepared using the dried spherulite powder under a pressure of 50 kg cm^{-2} at a temperature of 100 to 130°C could not be ultra-drawn and their λ_{max} was below 10.

CONCLUDING REMARKS

The influence of solution concentration on ultra-drawing in the GSP-method has been investigated using four kinds of gel-like spherulite formed from 1.0, 2.0, 4.0 and 6.0% w/w solutions of UHMW-PP. The following information was obtained.

(1) The volume of spherulites prepared from solutions below 4% w/w was linearly proportional to the polymer concentration in solution.

(2) The polymer concentrations in a gel-like spherulite formed from solutions below 6% w/w showed a fixed value of about 12% w/w. From this fact, the difference of chain entanglement density between gel-like spherulites was deduced to be very little.

(3) A GSP-sheet is composed of a multilayer structure formed by accumulation of lamellae and each lamella is well packed. The lamellar surface is uniformly rotating around the vertical axis to the surface of GSP-sheet, as it is parallel to the surface of above sheet.

(4) Very small differences were measured between λ_{max} values of GSP-sheets prepared from four kinds of gel-like spherulite, and of UHMW-PE[9] prepared by the GSP-method; values were considerably smaller than that for UHMW-PE prepared by the gel-casting method[14]. This fact characterizes the ultra-drawability of GSP-method, which is mainly due to the small difference of chain entanglement density between gel-like spherulites.

(5) The nominal stress-strain curve in the 1st stage of drawing (until $DR = 10$) seemed to be independent of initial

solution concentration, in contrast with that in the 2nd stage of drawing ($DR \geq 10$). This suggested that the effect of chain entanglement density on the stress-strain curve in the 1st stage of drawing was relatively little for the deformation by extension of folded polymer chains.

(6) The increase in strength and modulus with ultra-drawing was observed to be independent of initial solution concentration. This was considered to originate from the small differences between chain entanglement density among gel-like spherulites.

(7) The small difference of the chain entanglement density between gel-like spherulites is caused by disentanglement between polymer chains in an initial solution during formation of gel-like spherulites. Moreover, this small difference would be remained in GSP-sheet as a memory effect of chain entanglement density in an initial solution.

(8) The small difference of λ_{max} between GSP-sheets could be related to the yield stress (F) in the 2nd stage of drawing, and a linear relationship was established between λ_{max} and $F^{-1/2}$, as the same relationship was established for the GSP-sheet of UHMW-PE[9]. This relationship led to the ultra-drawing mechanism of GSP-sheet, which was explained as the deformation of three-dimensional networks composed of chain entanglement trapped in a gel-like spherulite.

(9) A value of $m = 0.31$ GPa$^{1/2}$ was obtained in Griffith plots; this was somewhat lower than the range of m in the gel-casting (or spinning) method for UHMW-PE[17], but is in good agreement with that for the gel-casting method for UHMW-PP[15]. From this fact, the size of crack (or defect) formed by compression of spherulites and neck deformation of GSP-sheet was assumed to be in the range of that in the gel-casting method for UHMW-PP.

It was concluded from the above information that ultra-drawing in the GSP-method progressed by deformation of three-dimensional networks composed of chain entanglements trapped in a gel-like spherulite, although there were no (or fewer) connections between gel-like spherulites used as a starting material. To make this more clear the influence of chain entanglement density on the ultra-drawing of UHMW-PP, and the difference of ultra-drawing behaviour between GSP-sheets and gel-casting sheets prepared from a solution of the same polymer concentration, should be compared in relation to their structural changes.

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