Ultra-drawing behaviour of ultra-high-molecular-weight polyethylene in the gel-like spherulite press method

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Ultra-drawing behaviour in the gel-like spherulite press method has been investigated using two kinds of gel-like spherulites formed from 1.0 and 2.0 wt% solutions of ultra-high-molecular-weight polyethylene. The influence of chain entanglement density in a solution on the increase in strength and modulus with ultra-drawing is discussed. An equation predicting the maximum draw ratio from the drawing stress of the predrawn specimens is presented. It is concluded that the influence on the ultra-drawing behaviour of the spherulite size and lack of chain connection between spherulites can be ignored in this processing method.

INTRODUCTION

High-performance polyethylene (PE) fibres, exceeding carbon and aramid fibres in strength and modulus, became available in the 1970s with the invention of fibrillar-crystal growing[1,2] and gel-spinning/casting methods[3,4]. Many studies have applied the processing principles of both methods to flexible polymers other than PE; high-performance fibres of high-molecular-weight poly(vinyl alcohol) (PVA) have consequently been developed[5,6]. In ultra-high-molecular-weight (UHMW) PE, there has been good progress in new processing methods for obtaining high-performance materials, i.e. the gel-like spherulite press method[7] subsequently referred to as the 'gel-press method'[8], single-crystal drawing[9,10], virgin-polymer-film drawing[11-13] and reactor-powder drawing[14].

In the ultra-drawing mechanism of the gel-spinning/casting method, the following results are noted.

1. The relation between the maximum draw ratio and the entanglement density between polymer chains can be explained by the deformation of a three-dimensional network composed of the entanglement points between polymer chains[15].
2. The increase in strength and modulus with ultra-drawing is independent of the drawing conditions, such as the state of gel (dry or wet) and temperature[16].
3. The increase in modulus with drawing agrees well with the theoretical curve, which is calculated using the molecular orientation function related to the draw ratio[17].

This suggests that ultra-drawing becomes possible in the gel-spinning/casting method, and leads to the attainment of ultimate properties by chain extension, based on the fact that the entanglement density between polymer chains is very low in comparison with that of usual methods such as melt spinning or solution spinning. A similar ultra-drawing mechanism may explain the high drawability in the gel-press method, single-crystal drawing and virgin-polymer-film drawing, because the entanglement density between polymer chains in these methods is lower than that of the gel-spinning method. However, as shown in *Figure 1*, the increase in modulus with ultra-drawing depends largely on the preparation conditions of the undrawn specimen, especially solution concentration: 2 wt% in gel spinning[16], 0.65 wt% in gel casting[18] and 0.1 wt% in single-crystal drawing[9]. Thus it is expected that the progress of chain extension with ultra-drawing is delayed more in the specimen with a lower chain entanglement density. However, the ultra-drawing mechanism has not yet been clarified from this point of view.

The gel-press method is distinct from the other methods in that gel-like spherulites formed from a semidilute solution of UHMW-PE are used: chain entanglements are introduced between lamellae in the gel-like spherulites, but there are no, or fewer, chain connections between spherulites[19]. There are no, or fewer, chain connections between lamellae in single-crystal, or virgin-polymer-film, drawing, and no spherulites in gel-spinning/casting. So, it is particularly interesting to elucidate the influence of entanglement density of polymer chains in a solution on the increase in strength and modulus in the gel-press method. In this paper, the ultra-drawing behaviour of
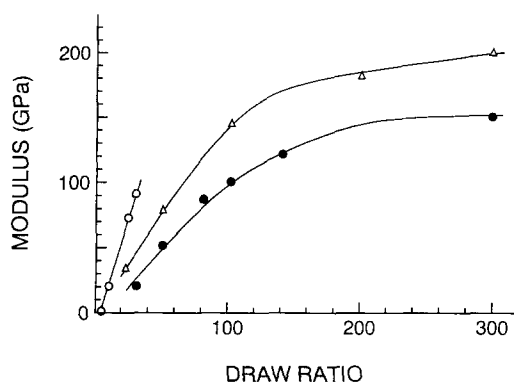

Figure 1   Increase in modulus with ultra-drawing in various processing methods: ○, gel-spinning method (2.0 wt%); △, gel-casting method (0.65 wt%); ●, single-crystal-drawing method (0.1 wt%). The values in parentheses show the polymer concentration in the initial solution

UHMW-PE in the gel-press method is investigated by using two kinds of gel-like spherulites formed from 1.0 and 2.0 wt% solutions of UHMW-PE. Since it was expected that the number of chain entanglements trapped in gel-like spherulites decreased during crystallization from solution, the cooling rate of solutions and the molecular weight of UHMW-PE were specified in this study.

EXPERIMENTAL

Preparation of gel-like spherulites

Two types of gel-like spherulites formed from 1.0 and 2.0 wt% solutions of UHMW-PE ($M_w = 2 \times 10^6$, HIZEX 240M) were used, because the upper limit of solution concentration, where gel-like spherulites of UHMW-PE formed separately, was in the range 2.0–2.5 wt%.

The 1 and 2 wt% solutions were prepared by heating dispersions of UHMW-PE powder in decalin to 160°C and holding for 30 min. Some 0.5 wt% of antioxidant (di-t-butyl-p-cresol) was mixed in the solution to stabilize the polymer. The gel-like spherulites were formed by cooling the solutions at a rate of about 1.5°C 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 1–3 min until the surface of the spherulites became cloudy, owing to removal of decalin from between the spherulites. A small amount (8–10 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°C min^{-1} to 100°C, holding for 10 min at this temperature, then heating again at 10°C min^{-1} from 100 to 200°C.

Preparation of gel-press sheet

A gel-press sheet was prepared by compressing some of the gel-like spherulite material under a pressure of 50 kg cm^{-2} at room temperature, and subsequently drying the decalin (30–35 wt%) contained in the compressed material under reduced pressure at room temperature. The obtained sheet was used as a specimen in this study, and contained 3–4 wt% decalin. The

specimens prepared from 1 and 2 wt% solutions were called A1 and A2, respectively. Both specimens were 0.5 mm thick and showed almost the same X-ray diffraction patterns with respect to the crystalline orientation (as shown in a previous paper[19]), namely that most lamellae were oriented with their surface parallel to the compression plane.

Preparation of drawn tape

The hot-drawing of specimens was carried out using a tensile tester equipped with an air oven. First, undrawn specimens, 20 mm long and 10 mm wide, were drawn to a length of 400 mm (draw ratio (DR) = 20) at a drawing speed of 10 mm min^{-1} at 100°C. Subsequently, this predrawn tape was cut into strips 60 mm long, which were again drawn to various lengths under the above drawing conditions. The drawing of specimens was carried out after preliminary heating at 100°C for 10 min. The decalin remaining in undrawn specimens (3–4 wt%) was evaporated in the first step of drawing to less than 0.1 wt%. The draw ratio was given as the denier-ratio of undrawn and drawn specimens, which corresponded well with that determined from the ratio of marking distance.

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 5 cm. In measuring the modulus of high-modulus specimens with a tensile tester, slight slippage in a chucking part may cause a large observational error, especially in the case of short specimens. 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. The agreement of dynamic and tensile modulus was confirmed using a gel-spun fibre of UHMW-PE.

RESULTS AND DISCUSSION

Formation and properties of gel-like spherulites

Figures 2 and *3* show optical and polarized microscopic photographs, respectively, of the gel-like spherulites prepared from 1 and 2 wt% solutions. Both types of spherulite show a similar morphology, with fibril-like lamellae growing parallel to the radial direction of the spherulite. However, they differ in size: spherulites from the 1 wt% solution are 60–70 μm in diameter, while those from the 2 wt% solution are 80–90 μm. The volume ratio of the former to the latter was calculated at nearly 1:2 from the ratio of diameters; this value corresponds well to the polymer concentration ratio in the initial solutions. This suggests that the formation rate of primary nuclei from a semidilute solution is almost constant, irrespective of the polymer concentration; the growth rate of spherulite volume is linearly proportional to the polymer concentration; and the polymer concentration in a gel-like spherulite is independent of the initial solution concentrations.

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 pushed. Thermogravimetric curves of the spherulites, after
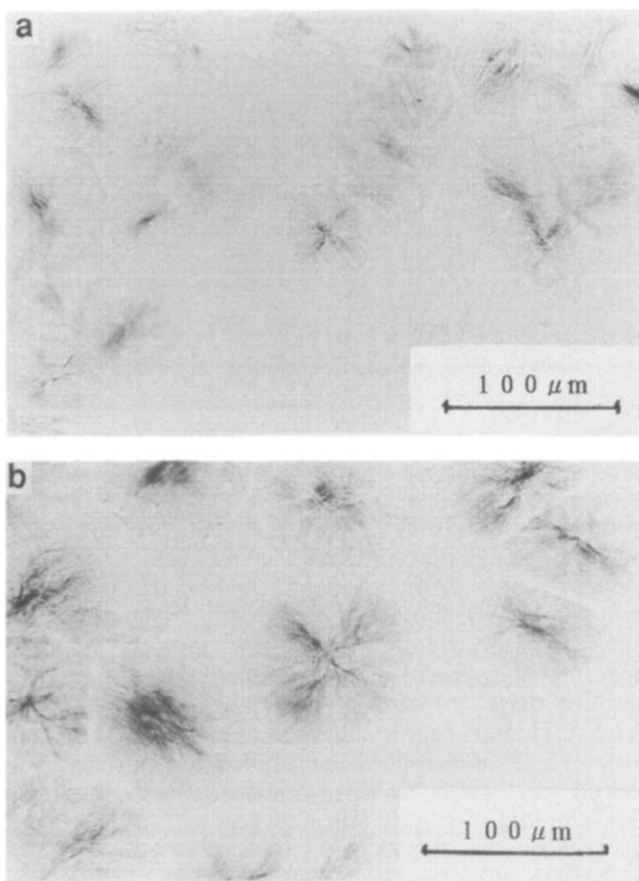
Figure 2 Optical microscopic photographs of the gel-like spherulites formed from (a) 1 wt% and (b) 2 wt% solutions
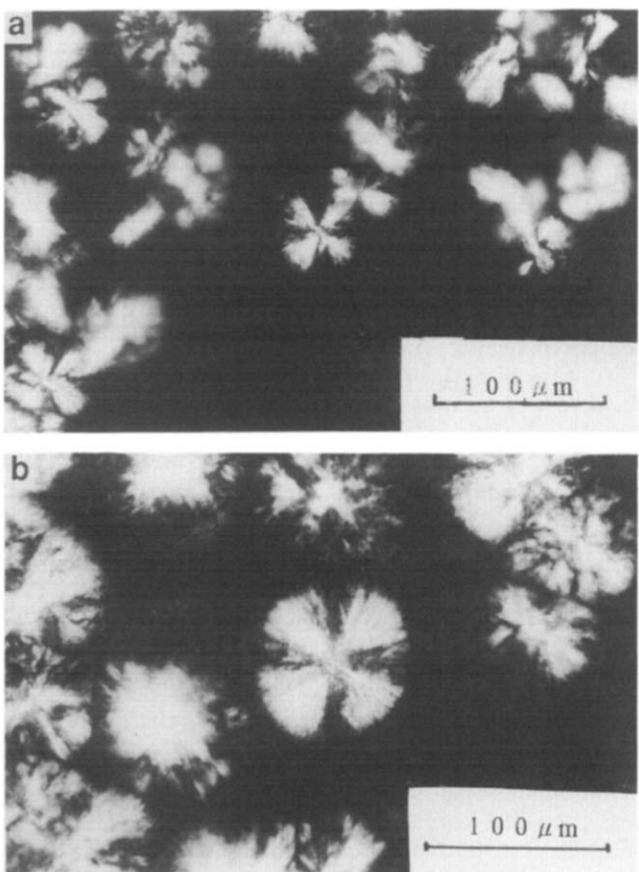

Figure 3 Polarized microscopic photographs of the gel-like spherulites formed from (a) 1 wt% and (b) 2 wt% solutions

removal of the decalin from between them, are shown in *Figure 4*. Gel-like spherulites formed from both 1 and 2 wt% solutions show the same evaporation behaviour of decalin: *Figure 4* indicates that the decalin contents in the gel-like spherulites are 89.7 and 90.7 wt%, respectively. This indicates that the polymer concentration in a gel-like spherulite is about 10 wt%, independent of the initial solution concentration.

Increase in strength and modulus by ultra-drawing

In the hot-drawing at 100°C of specimens A1 and A2, clear neck deformation was observed. The draw ratios in the necking parts were the same for both specimens and were in the region of 10 ± 0.5. The decreasing ratios of thickness and width as a result of necking were 86% and 22%, respectively. Considering that the gel-press sheet is composed of a stack of lamellae, as shown in a previous paper[19], this necking phenomenon is inferred to be due mainly to the extension of folded polymer chains in neck deformation. An apparently uniformly drawn tape, 0.04 mm thick and 6.8 mm wide, was obtained at DR = 20.

The increase in strength and modulus with ultra-drawing was investigated by the second hot-drawing at 100°C of the tapes predrawn to a total draw ratio (tDR) of 20. The results are shown in *Figure 5*. A linear relation of strength and modulus *versus* tDR was obtained for tDR < 60. The slopes of modulus and strength gradually decline from tDR = 60 as the tDR increases, and exhibit a plateau at tDR > 100. Consequently, a strength of 3.5 GPa and modulus of 170 GPa were attained, which were considerably lower compared with a strength of 4.5 GPa and modulus of 200 GPa found in a previous paper[19]. This difference is probably due to the different drawing conditions used: die-drawing in the first step and continuous two-step hot-drawing were used in ref. 19, and draw ratios and drawing temperatures were different in each step.

The increase in strength and modulus per unit increase in draw ratio (GPa DR^{-1}) at tDR < 60 is the same in specimens A1 and A2: 0.046 GPa DR^{-1} for strength and 1.8 GPa DR^{-1} for modulus. Both values are considerably lower than the corresponding values of 0.069 and 2.7 GPa DR^{-1} for the gel-spun fibre from 2 wt% solution of UHMW-PE $(M_w = 2 \times 10^6)$[20]. The effect of molecular orientation in the gel-spun fibre can be ignored, because it is almost the same as the effect in the gel-cast film from 2 wt% solution of UHMW-PE $(M_w = 2 \times 10^6)$[21].
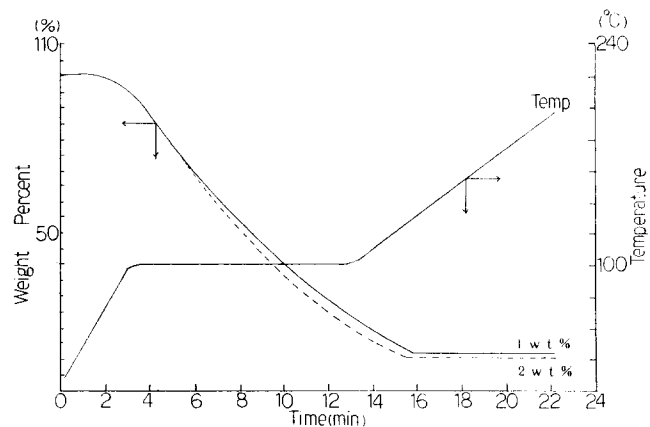

Figure 4 Thermogravimetric curves of the gel-like spherulites formed from 1 wt% (— —) and 2 wt% (- - -) solutions
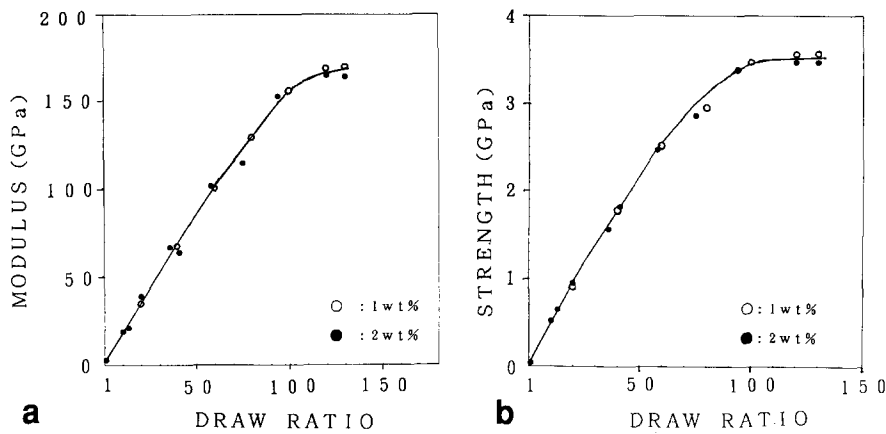
Figure 5 The increase in modulus (a) and strength (b) with ultra-drawing in gel-press sheets prepared from 1 and 2 wt% solutions
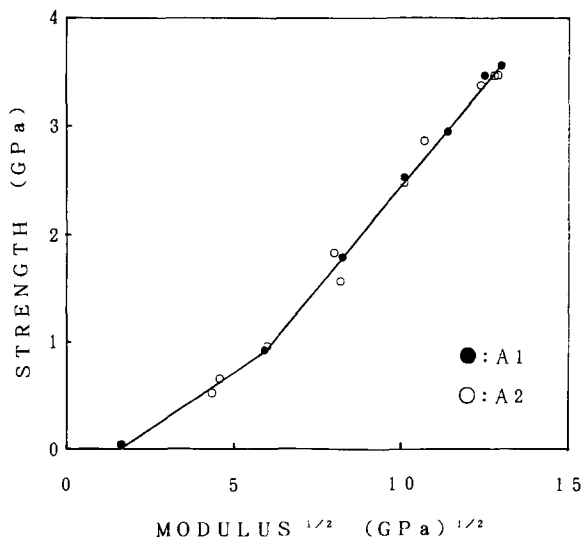

Figure 6 Griffith plots on the drawn tapes prepared from gel-press sheets of A1 and A2

Hence, the difference between the two processing methods is considered to be caused by the following mechanisms.

1. The gel-press method is different from the gel-spinning method in that the gel-press sheet consists of a stack of lamellae in gel-like spherulites, but there are no (or fewer) chain entanglements between lamellae belonging to other spherulites. Hence, it is predicted that slip along the boundaries between lamellae belonging to adjacent spherulites will arise during ultra-drawing.

2. The chain entanglement density in the gel-press sheet is considered to be lower than that in the gel-spun fibre, because disentanglement between polymer chains takes place during formation of the gel-like spherulites from solution. Thus it is predicted that the transfer efficiency of the drawing stress between polymer chains is reduced in the gel-press sheet, and hence the progress of molecular orientation and chain extension by drawing will be delayed.

As shown in *Figure 5*, the increase in strength and modulus with ultra-drawing was independent of initial solution concentration in both specimens A1 and A2. This indicates that doubling the chain entanglement density in solution scarcely affects the strength and modulus behaviour. It is deduced from this that the disentanglement between polymer chains in solution takes place during formation of the gel-like spherulites

from solution, and consequently the numbers of entangled polymer chains connecting lamellae in a gel-like spherulite are remarkably close, although the spherulites are grown from solutions of different concentration, i.e. 1 and 2 wt%.

The ultra-drawing in the gel-press method is possible only after the gel-like spherulite material is compressed, because there are no (or fewer) connections between them[19]. This fact suggests that cracks along the boundary surfaces between lamellae belonging to adjacent spherulites should be formed by ultra-drawing. *Figure 6* shows Griffith plots of gel-press sheets A1 and A2, drawn using the data in *Figure 5*. In the Griffith theory, the relation of strength (σ) and modulus (E) is shown by the equation $\sigma = mE^{1/2}$, in which m is inversely proportional to the square root of crack size. Griffith plots of high-modulus PE fibres prepared by various methods were shown in a previous paper[22]. A value of m can be determined in the region of $E > 13$ GPa and depends largely on the processing method. In the gel-press sheets A1 and A2, $m = 0.37(\text{GPa})^{1/2}$ was obtained in the region of $E > \sim 36$ GPa, which is in the range of m for the gel-spinning method and the fibrillar-crystal-growing method. This shows that cracks along the boundary surfaces between lamellae belonging to adjacent spherulites are hardly formed by ultra-drawing. From the above information, it is deduced that the lower entanglement density of polymer chains in gel-press sheets is responsible for the considerably lower increase in strength and modulus in the gel-press method compared to that in the gel-spinning method.

Prediction of maximum draw ratio from drawing stress

Stress–strain curves at 100°C for both predrawn tapes with DR = 20 are shown in *Figure 7*. The maximum drawing stress (F) of specimen A1 around the yield point (144 MPa) is a little lower than that of specimen A2 (164 MPa) and the maximum draw ratio (λ_{max}) of specimen A1 (143) is a little higher than that of specimen A2 (136). From this observation, we tried to predict λ_{max} from the value of F for a predrawn tape, and consequently found the following relation to hold:

$$\lambda_{max} = k(1/F)^{1/2} \qquad (1)$$

This relation is recognized over the whole data range, including the results of predrawn specimen of gel-cast films prepared from 1 and 2 wt% solutions of UHMW-PE ($M_w = 2 \times 10^6$), i.e. the constant k is the same for both processing methods[23] and is also applicable to the predrawn specimens of UHMW polypropylene in the gel-press method[21]. In equation (1), the constant k
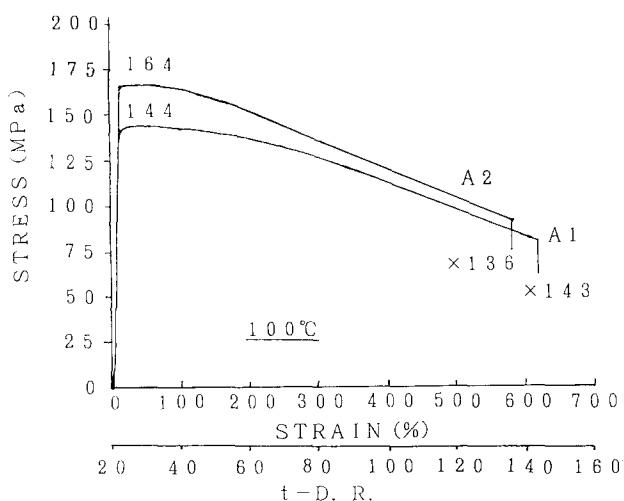
Figure 7 Stress–strain curves of predrawn tapes with DR = 20 from gel-press sheets of A1 and A2, measured at 100°C under a deformation rate of 50% min⁻¹

depends mainly on the draw ratio of a predrawn specimen.

It is considered that the crystalline parts in a predrawn specimen can no longer play a cross-linking role such as in rubber elasticity deformation during hot-drawing at 100°C, which corresponds to the crystalline dispersion temperature of PE[24]. It is suggested that only the chain entanglements play a cross-linking role in the drawing deformation at 100°C. Therefore, we can assume that the drawing stress arises in proportion to the chain entanglement density in a predrawn specimen. By this simple assumption, $(1/F)$ in equation (1) arises in proportion to $1/\rho$ (where ρ = chain entanglement density) and hence in proportion to the contour length (L) of the chain segment between entanglement points. So the following equation is deduced:

$$\lambda_{max} \propto L^{1/2} \qquad (2)$$

Equation (2) is well known as the relation of λ_{max} and L in the classic theory of rubber elasticity[25]. This suggests that the ultra-drawing of a gel-press sheet can be treated mainly as the deformation of three-dimensional networks composed of chain entanglements trapped in a gel-like spherulite, in spite of no (or fewer) connections between gel-like spherulites. It is further inferred that a type of chain connection between lamellae belonging to the different spherulites is formed, while much decalin (about 30 wt%) contained in the compressed material of gel-like spherulites is removed in the drying process.

Considering the preparation conditions of specimens A1 and A2, the ratio of chain entanglement density in both predrawn specimens is found to be close to 1:1.14, rather than the value of 1:2 in solution. In this way, we can explain that the increases in strength and modulus with ultra-drawing are the same in both specimens, as shown in *Figure 5*.

CONCLUSIONS

The ultra-drawing behaviour in the gel-press method was investigated by using two kinds of gel-like spherulites formed from 1 and 2 wt% solutions of UHMW-PE. The following information was obtained.

1. The increase in strength and modulus with ultra-drawing was observed to be independent of initial

solution concentration. This was deduced to be due to a small difference of the chain entanglement density between the two kinds of gel-like spherulites, which was caused by disentanglement between polymer chains during crystallization from solution.

2. The slope of the Griffith plot was in the same range as those of the gel-spinning method and of the fibrillar-crystal-growing method.

3. The slopes of increasing strength and modulus in the gel-press method were considerably lower in comparison with those in the gel-spinning method, owing to the lower chain entanglement density in a gel-like spherulite.

4. The maximum draw ratio can be predicted from the drawing stress at 100°C of a predrawn specimen.

From the above information, it was concluded that the influence on the ultra-drawing behaviour of the size of spherulites and of no (or fewer) chain connections between each spherulite could be ignored.

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