High-performance materials from gel-like spherulites of ultra-high-molecular-weight polyethylene*

T. Ohta†, F. Okada, M. Hayashi and M. Mihoichi
Toyobo Co. Ltd, Research Center, 2-1-1 Katata, Ohtsu, Shiga 520-02, Japan
(*Received 9 January 1989; revised 22 March 1989; accepted 31 March 1989*)

A new method using gel-like spherulites will be presented for obtaining high-performance materials of ultra-high-molecular-weight polyethylene (UHMW-PE), which is available for the production of high-strength and high-modulus materials having a large cross-sectional area, for example, rods and thicker tapes. Such high-performance organic materials were not known until the development of this method in 1983. Ultra-drawability and characteristics of UHMW-PE produced by this method are discussed, based on the fine structure of gel press sheet.

(Keywords: gel-like spherulite; ultra-high-molecular-weight polyethylene; high modulus; high strength; large cross-sectional material; gel press sheet; gel press method)

INTRODUCTION

There have been many studies on processing methods[1] for obtaining high-performance synthetic fibres since polymer single crystals were found in 1957[2]. All of these efforts are nothing but attempts to attain a high degree of chain extension and alignment of longer chain molecules in the direction of the fibre axis for utilizing effectively the ultimate strength of their molecules. There are two major routes depending on starting materials, that is, intrinsically rigid or flexible polymers. One is a method to prevent chain folding by using rigid polymers, as represented in aramid fibres. The other is a method to extend folded chains formed during formation of the fibre. In the latter case many attempts have been carried out on various flexible polymers, but it was very difficult to make high-performance fibre from them. However, in 1975–76 high-performance polyethylene fibre exceeding Kevlar in strength and modulus was developed by a fibrillar crystal growth method[3] and a gel spinning method[4]. At present, only the gel spinning method has been adopted as a method for industrial production.

In this paper a new method using gel-like spherulites will be presented for obtaining high-performance drawn materials of ultra-high-molecular-weight polyethylene (UHMW-PE), which was developed in 1983 under the following background[5]. As shown in *Figure 1*, even in the gel spinning method, tenacity and modulus rapidly decrease with increasing diameter of the single filament up to 100 μm[6]. On the other hand, high-performance plastic rod is required as a replacement for steel wire, because the latter has some essential problems such as heavy weight, corrosion, electromagnetic interference, etc. Hence, several kinds of plastic composite rods reinforced by glass fibre or aramid fibre are used. Development of polyoxymethylene (POM) rod is also in progress[7]. Along these lines, high-performance PE rods having a diameter of around 1.0 mm have been developed by using gel-like spherulites of UHMW-PE[5].

GEL PRESS METHOD

A new method using gel-like spherulites is characterized by ultra-drawing of a pressed sheet formed by compression of an accumulated material of gel-like spherulites obtained from semi-dilute solution of UHMW-PE. The gel-like spherulites were prepared with 2% decalin solution of UHMW-PE ($M_w = 2 \times 10^6$, Hizex 240 M). As shown in *Figure 2*, many spherulites are easily formed by cooling of this solution.

Each spherulite shows gel-like behaviour due to inclusion of a large amount of the solvent, about 90%. Hence, we call them 'gel-like spherulites'. An accumulated material of them was prepared by filtration of a dispersion in decalin. By applying a very small strain to it, a crack as shown in *Figure 3* easily arises. A gel-like spherulite having a diameter of about 80 μm can be observed along the crack, whose inner part is transparent because it contains much solvent in it. This means that there are no connections between each gel-like spherulite. However, by giving a compression of about 50 kg cm^{-2} to it at room temperature, the pressed sheet starts to show ultra-drawability up to a total draw ratio of 100–200, which contains 20–30% solvent. From this fact, we call this sheet 'gel press sheet' and this processing method 'gel press method'.

DISCUSSION ON ULTRA-DRAWABILITY OF THE GEL PRESS SHEET

Ultra-drawability of the gel press sheet would be considered to be due to adhesion between each gel-like spherulite by removing most of the solvent from it and reorientation of lamellae in it during compression, because re-entanglements between polymer chains in

---

* Presented at the Annual Meeting of 2nd SPSJ International Polymer Conference, Tokyo, 1986

† Present address: Faculty of Science of Living, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-Ku, Osaka 558, Japan and to whom correspondence should be addressed

0032-3861/89/122170–04$03.00

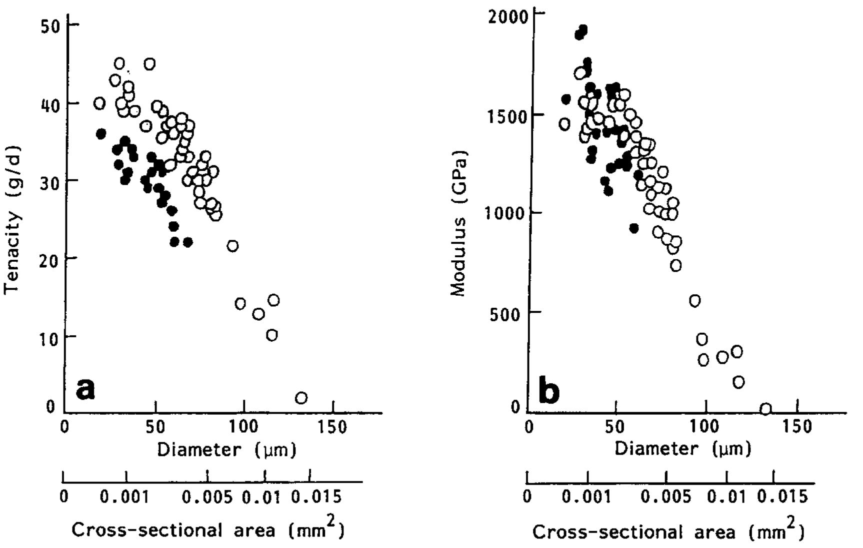

Figure 1 Diameter dependence of (a) tenacity and (b) modulus in HP-PE fibres by gel spinning method (from Allied Patent[6]). ○, Monofilament; ●, multifilament

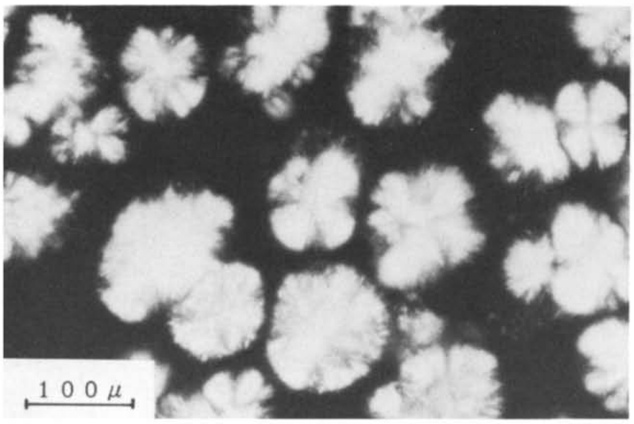

Figure 2 Gel-like spherulites obtained by cooling a semi-dilute solution

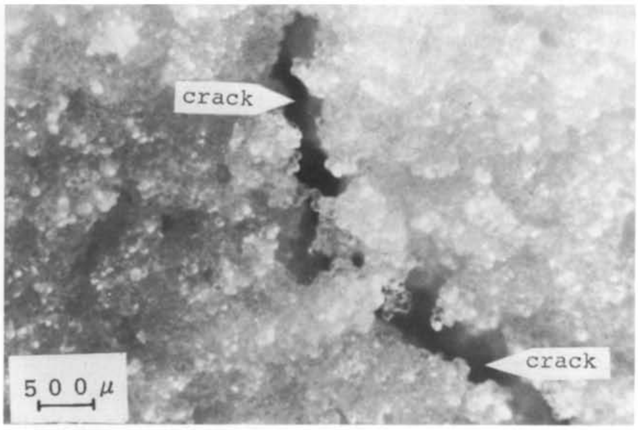

Figure 3 Accumulated material of gel-like spherulites before pressing

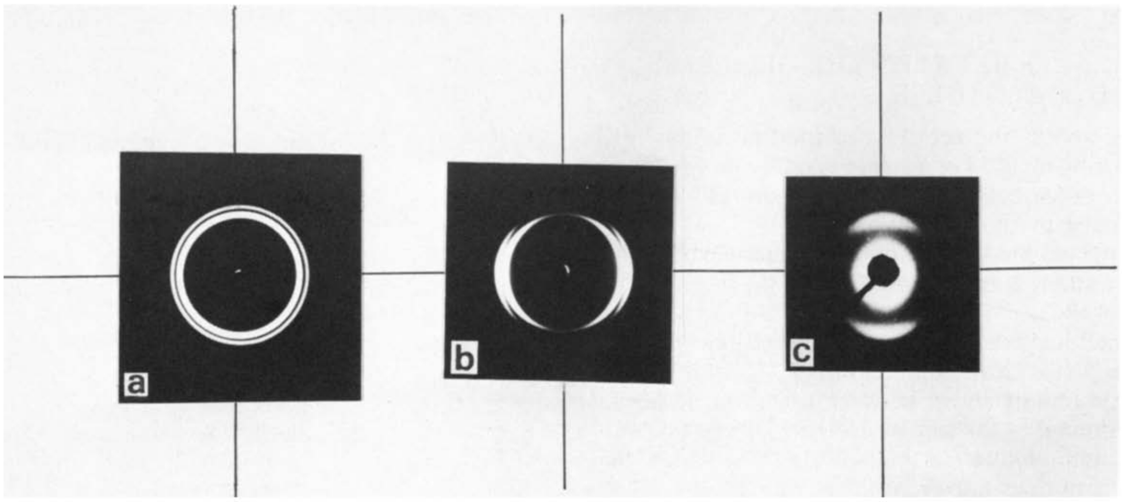

Figure 4 WAXD and SAXS of a gel press sheet (surface is parallel to the horizontal axis): (a) through pattern of WAXD; (b) edge pattern of WAXD; (c) edge pattern of SAXS

lamellae belonging to different spherulites are difficult at room temperature.

Figure 4 shows WAXD and SAXS patterns of a gel press sheet after extracting the solvent with n-hexane, whose surface is parallel to the horizontal axis. The through pattern of WAXD shows strong diffraction rings from the (110) and (200) crystal planes. The edge pattern of WAXD shows preferential orientation of the (110) and (200) crystal planes in the horizontal direction. This indicates that the lamellar surface is uniformly rotating around the vertical axis to a gel press sheet and is oriented parallel to its surface. In the edge pattern of SAXS, strong

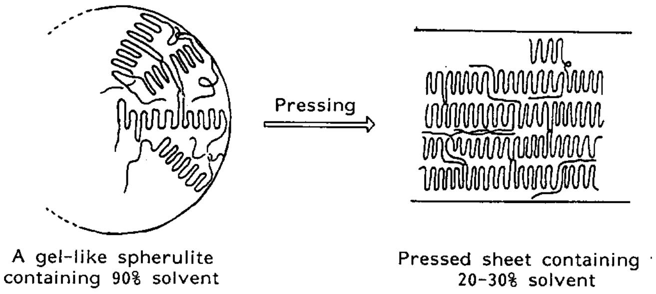

Figure 5 Structural model of the change of lamellar packing

interference from long-period structure of about 120 Å can be observed in the vertical direction, which corresponds to the lamellar thickness. This indicates that a gel press sheet is composed of a multilayer structure formed by accumulation of lamellae and each lamella is well packed. Such a structure of the gel press sheet would be given by reorientation of lamellae in a gel-like spherulite during compression, as shown in *Figure 5*. Each lamella grown in the radial direction of a spherulite reorients so that the lamellar surface may orient parallel to the plane of compression under torque given by a compression. Such structure is similar to that of a single-crystal mat[8] and of a thin film cast from dilute solution of about 0.5% concentration[9].

All of these samples show ultra-drawability, having a total draw ratio (*TDR*) of 100–300, which is much higher than that (*TDR* = 30–50) of a gel fibre from solution spinning of a 2% concentration of UHMW-PE ($M_w = 2 \times 10^6$)[10]. In the case of a gel press sheet, the same solution of UHMW-PE as the above gel fibre is used, so the degree of chain entanglement in both samples is inferred to be almost the same. Therefore, ultra-drawability of the gel press sheet would be considered to be due to formation of a structure having a high degree of regularity, i.e. regular chain folding in a lamella, regular orientation of lamellae.

DIFFERENCES BETWEEN THE GEL PRESS METHOD AND OTHERS

From the above, the gel press method is similar to the ultra-drawing method of a single-crystal mat (SCM) and a thin film cast from dilute solution (TF), but is characterized by the following facts.

(1) In the gel press method, chain entanglements have been introduced between lamellae in a gel-like spherulite because of the use of a semi-dilute solution, but there is no chain entanglement between each gel-like spherulite. The latter fact is clearly different from TF. In SCM there is no chain entanglement between each lamella because a single crystal is formed by isothermal crystallization from a dilute solution of below 0.1%[8] in which chain entanglement does not occur[9].

(2) The ascending rate of strengths and moduli with increase of draw ratio is higher in gel press sheet than in SCM[11], which would be due to the existence of chain entanglements in gel press sheet. Moreover, this consideration would be supported by the fact that a similar phenomenon has been observed in the drawing behaviour of gel film or gel fibre, depending on the polymer concentrations in solution casting or spinning[12].

(3) By using gel-like spherulites it is easy to prepare a thick gel press sheet having macroscopically and microscopically homogeneous structure, and consequently high-performance polyethylene (HP-PE) materials having a large cross-sectional area, such as rods and tapes, can be produced.

Recently, the preparation of high-modulus rod by using single-crystal aggregates of UHMW-PE has been reported[13], but practically the major problem in the method using them or SCM is that the solution for preparation of single crystals is too dilute. In the case of TF it is difficult to form a homogeneous structure in it with increase of its thickness, i.e. formation of spherulites in core layer, and so on.

By the gel press method high-performance tapes and rods having a large cross-sectional area of above 0.018 mm^2 can be obtained[5]. In the case of tapes, ultra-drawing up to a total draw ratio (*TDR*) of 150–200 can be done by hot drawing of a pressed sheet and consequently a strength of 4.5 GPa and a modulus of 200 GPa can be attained. In the case of rods, ultra-drawing up to a *TDR* of above 100 can be done by die drawing and continuously hot drawing of the pressed sheets, and consequently a strength of above 2 GPa and a modulus of 150 GPa can be attained.

DIAMETER DEPENDENCE OF STRENGTH AND MODULUS IN HP-PE ROD

HP-PE rods having a diameter of 0.5 to 1.0 mm were prepared by ultra-drawing (*DR* = 140) of the gel press sheet, that is, die drawing of *DR* = 8 at 110°C and continuous two-step drawing of *DR* = 18 at 120°C and 130°C. The relation between modulus, strength and diameter of HP-PE rods obtained by this method is shown in *Figures 6* and 7 in comparison with that by the gel spinning method, and that of POM rods[14] and a composite rod of Kevlar/epoxy. It is found that even in the gel press method the moduli attained decrease with increase of diameter and at a diameter of 1.0 mm the modulus of 150 GPa can be attained, which is more than three times higher than that of POM rods and of the

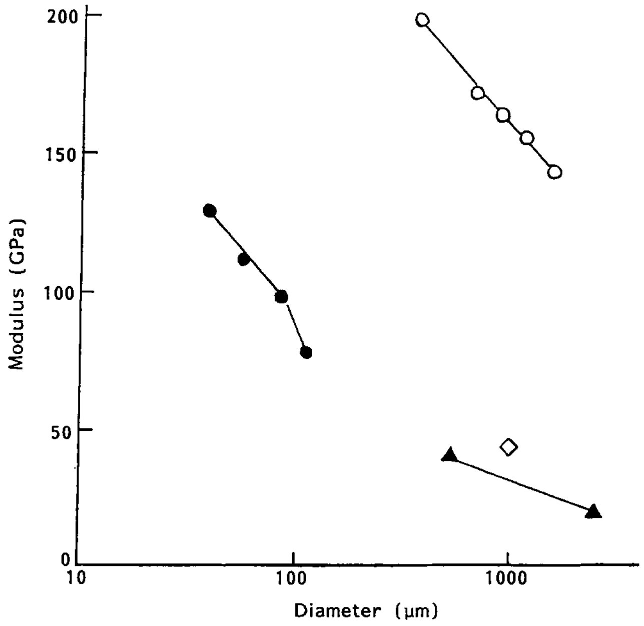

Figure 6 Modulus vs. diameter. ○, gel press-drawing of PE; ●, gel spinning-drawing of PE; ▲, pultrusion of Kevlar-epoxy (4/6); ◇, dielectric heating of POM

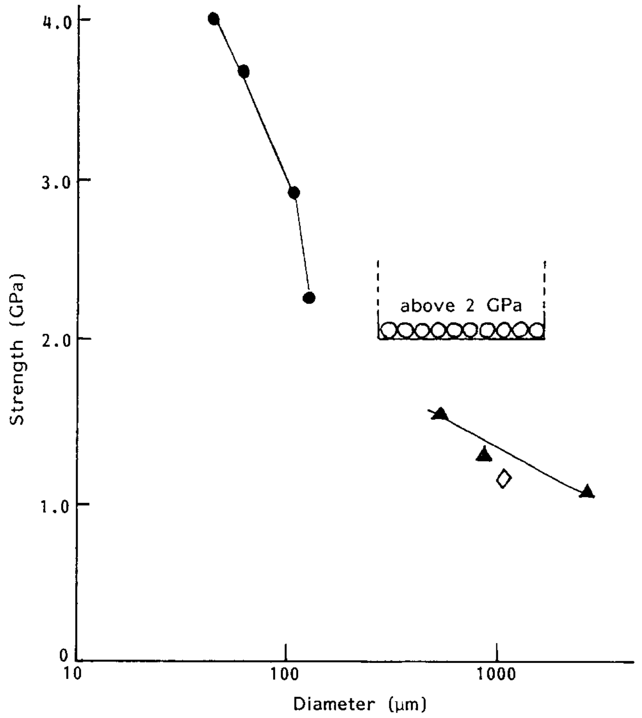

Figure 7 Strength vs. diameter. For symbols see *Figure 6*

Kevlar/epoxy composite rod. On the other hand, the strengths of HP-PE rods having a diameter of around 1.0 mm are about 2 GPa. However, this is the breaking strength observed when the chucking part was broken in a test piece and it is not the true value. As exact measurement of the strength is very difficult due to the large diameter of it, the true value should be considered to be more than 2 GPa since the strength of HP-PE tapes made by the gel press method are related linearly to the modulus. This linear relationship has been shown in HP-PE fibres by the gel spinning method[15]. One may consider that the major reason for this relationship is that strength and modulus will be proportional to the amount of chain extension by ultra-drawing, but full investigation of this matter will remain for future work.

CONCLUSIONS

High-strength and high-modulus materials of UHMW-PE having a large cross-sectional area can be produced by the gel press method using gel-like spherulites obtained from solution, and which cannot be obtained by the gel spinning method. This method is available for the production of high-performance PE rods, which would be due to the macroscopically and microscopically homogeneous structure of a gel press sheet.

REFERENCES

1 Ohta, T. *Polym. Eng. Sci.* 1983, **23**, 597
2 Keller, A. *Phil. Mag.* 1957, **2**, 1171
3 Zweinenburg, A. and Pennings, A. *Colloid Polym. Sci.* 1975, **253**, 452
4 Smith, P. and Lemstra, P. J. *Macromol. Chem.* 1976, **180**, 2983
5 Ohta, T. and Okada, F. US Patent 4 643 865 (1987), Toyobo Co. Ltd
6 Kavesh, S. and Prevorsek, D. C. US Patent 4 413 110 (1983), Allied Corp.
7 Nakagawa, K., Maeda, O. and Yamakawa, S. *J. Polym. Sci., Polym. Lett. Edn.* 1983, **21**, 933
8 Miyasaka, K. *et al. Polym. Prepr. Japan* 1983, **32**, 873; Kanamoto, T. *et al. Polym. Prepr. Japan* 1983, **32**, 741
9 Matsuo, M. *et al. Polym. J.* 1986, **18**, 741
10 Ohta, T. and Okada, F. unpublished
11 Ohta, T. *et al. Polym. Prepr. Japan* 1988, **37**, 1228
12 Smith, P., Lemstra, P. J. and Booij, H. C. *J. Polym. Sci., Polym. Phys. Edn.* 1981, **19**, 877; Ohta, T. and Okada, F. unpublished
13 Kanamoto, T. *et al.* Preprints of 2nd SPSJ International Polymer Conference, Tokyo, 1986, p. 5
14 Ishida, S. *Senigakkaishi* 1987, **43**, 143
15 Smith, P. and Lemstra, P. J. *Polymer* 1980, **21**, 1341