Micro-Structure and Characteristics of Highly Oriented Polyoxymethylene obtained by Press and Biaxial Drawing

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Received 18 November 2004; accepted 28 March 2005
DOI 10.1002/app.22693
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The physical structure of oriented polyoxymethylene (POM) drawn in two steps by press drawing and subsequent simultaneous biaxial drawing was studied. The degree of crystallinity, the orientation, and the tensile modulus depending on draw ratio were analyzed. By the press drawing method, the draw ratio reached 6.0, the tensile modulus was 4.5 GPa, and the degree of crystallinity decreased from 70% to 65%. By the two-step drawing of press drawing followed by subsequent simultaneous biaxial drawing, the tensile modulus reached 11 GPa when the draw ratio was 14 times, and the degree of crystallinity increased from 71% to 76–80%, but it did not depend on the draw ratio, and showed effectively a constant value (average 77%). The physical structural properties, such as the degree of crystallinity, the orientation of the crystal, and the lamella structure, were analyzed by SEM, X-ray diffraction, and other methods. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 835–844, 2005

Key words: polyoxymethylene; films; drawing; orientation; crystal

INTRODUCTION

Polyoxymethylene (POM) is one of the five major engineering plastics and its production rate is about 600,000 tons worldwide and 83,000 tons in Japan per year. It is mainly utilized in mechanical parts and shows excellent performance against wear in particular. It is a useful material in the plastic industry because it is easily prepared from formaldehyde and has a simple chemical structure, in addition to its excellent characteristics. Many kinds of parts made with POM are used for various purposes, but few applications of its film are known.

Geil, Clark, Bahadur and their coworkers studied the drawing of the film[1,2,3] and found that the preparation of the drawn films was very difficult because the crystal structure in the POM film changed during the drawing.

In our previous paper[4], the draw ratio by the press drawing reached 6.0 and the tensile modulus increased from 2.5 GPa to 4.5 GPa. However, the degree of crystallinity decreased slightly. The rupture elongation increased in the lower drawing region and it peaked when the draw ratio was 1.7. The film pressed by 2 times was drawn by the biaxial drawing machine. The high tensile modulus was obtained and the maximum value was 11 GPa at 14 times of the draw ratio. The lamella structure of POM was supposed to loosen and was oriented along the drawing axis by the first pressing. The lamella was highly oriented by the second drawing procedure.

The purpose of this study is the analysis of the crystal structure of the film that is drawn by a press and a simultaneous biaxial drawing machine.

EXPERIMENTAL

Materials used

The POM used in this study was a linear homopolymer manufactured by Asahi Chemical (grade No. TENAC 3010). The outline of the preparation is as follows.

$$\mathrm{CH_2O} \xrightarrow[\text{Catalyst}]{\text{Polymerization}} \mathrm{HO \cdot (CH_2O)n \cdot H} \text{ (unstable)}$$

$$\xrightarrow[\text{End Capping}]{\text{(CH3CO)2O}} \mathrm{CH3COO{-\!\!-}(CH_2O) \cdot n \cdot COCH3} \text{ (stable)}$$

The molecular weight was 60,000 (M_n), 225,000 (M_w) and the ratio of M_w/M_n is 3.75. The peak temperature of the melting measured by DSC (manufactured by Seiko, DSC-100) was 177.5°C. To obtain a sheet of 0.70 mm thickness and 150 mm width, the POM was

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Journal of Applied Polymer Science, Vol. 99, 835–844 (2005)

melted at 200°C to cast onto twin cooling rolls at 135°C.

Drawing methods

Press drawing

Two kinds of drawing methods were applied. The press drawing, where one of the presses was for heating and the other for cooling, was used as the first step. The specifications of the press were (1) the size of the press board was 400 mm × 400 mm, (2) the temperature range was 25–250°C, and (3) the maximum pressure was 50 tons by manually operated mechanism.

Five sheets and boards, namely (1) an electroplated steel plate, (2) PMMA board (10 mm thickness), (3) nondrawing polypropylene (PP) (4) POM sheet, (5) nondrawing PP (6) PMMA board (10 mm thickness) and (7) a electroplated steel plate, were put between the two press boards.

After the temperature was elevated from 25°C to 150°C, the specimen was held for 10 min at 150°C under 1.5 MPa. The temperature of the POM sheet rose up to 135°C. The POM sheet was quickly moved to the cooling boards in less than 10 s and drawn to the desired temperature under 20 MPa.[5] The advantage of the press method is that a sheet can be uniformly and smoothly drawn by sliding on the surface of the electroplated steel sheets.

Simultaneous biaxial drawing

For further drawing, the sheet was moved to the drawing machine to be simultaneously drawn by mechanical means. The temperature for this second drawing was set at 170°C.

Measurement of draw film

The degree of the crystallinity was measured by density method. It was calculated by eq. (1) using the density (d) of the film measured by the density gradient tube filled with n-heptane and carbon tetrachloride at 23°C.

$$D = d_c(d - d_a)/[d(d_c - d_a)] \times 100(\%) \qquad (1)$$

where d_c is the density of the crystal (1.506 g/mL) and d_a is the density of the amorphous phase (1.250 g/mL). A polarizing microscope equipped with an orthogonal polarizer was used for the visual observation of the crystalline super structure.

Generally speaking, there is room for error in the density method to measure the degree of crystallinity, because deformed materials include void.[5] The preliminary tests had been carefully done. A good correlation between the results from the density method and the heat of fusion of the crystal was obtained.[6] It was considered that the generation of voids was restrained by the press procedure.

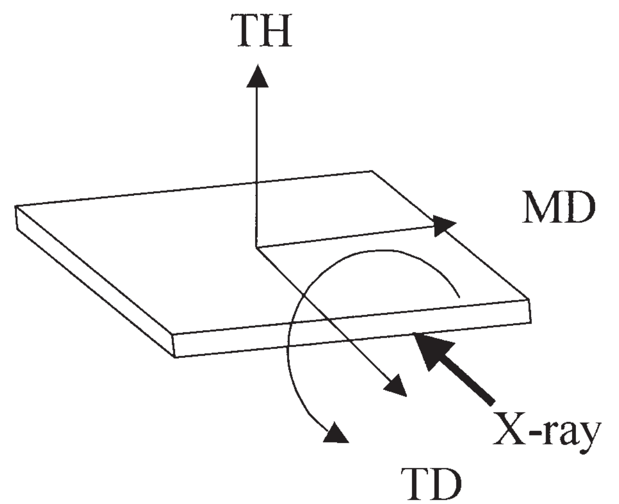

Figure 1 Incident direction of X-ray and three directions (TH, TD, and MD).

The tensile modulus of elasticity was calculated along with the tensile strength, and the elongation of the specimen (rectangle: 100 mm length, 10 mm width) was measured by a tensile tester in the atmosphere (temperature = 23°C, humidity = 60%). The length of the clamps was 60 mm and the speed of the head was 30 mm/min.

X-ray diffraction was utilized for following the presence of crystallinity and its orientation. An XD-3A diffraction apparatus manufactured by Shimadzu Co. was used. The source of X-ray was the filtered Cu Kα line of Ni and the strength was 30 kV and 28 mA. The monochromater for the WAXD photo was used to improve accuracy by cutting the Kα line, because the Kβ line disturbs the measurement when the strength of the X-ray increases in the case of the Cu Kα line of Ni.[7]

X-ray photos were taken along the three orthogonal axes parallel to TH, TD, and MD as depicted in Figure 1 with a flat camera. To observe the orientation by measuring the diffraction intensity from the POM (100) face, the angle was adjusted to that of POM (100) (2θ = 22–23.5°) and subsequently the plate was rotated by 4° per minute.

RESULTS AND DISCUSSION

Crystal structure after press drawing

In general, the degree of crystallinity of POM is 60–80% and the shape is spherical (spherulite). The size of spherulite is 10–50 μm and the larger spherulite of

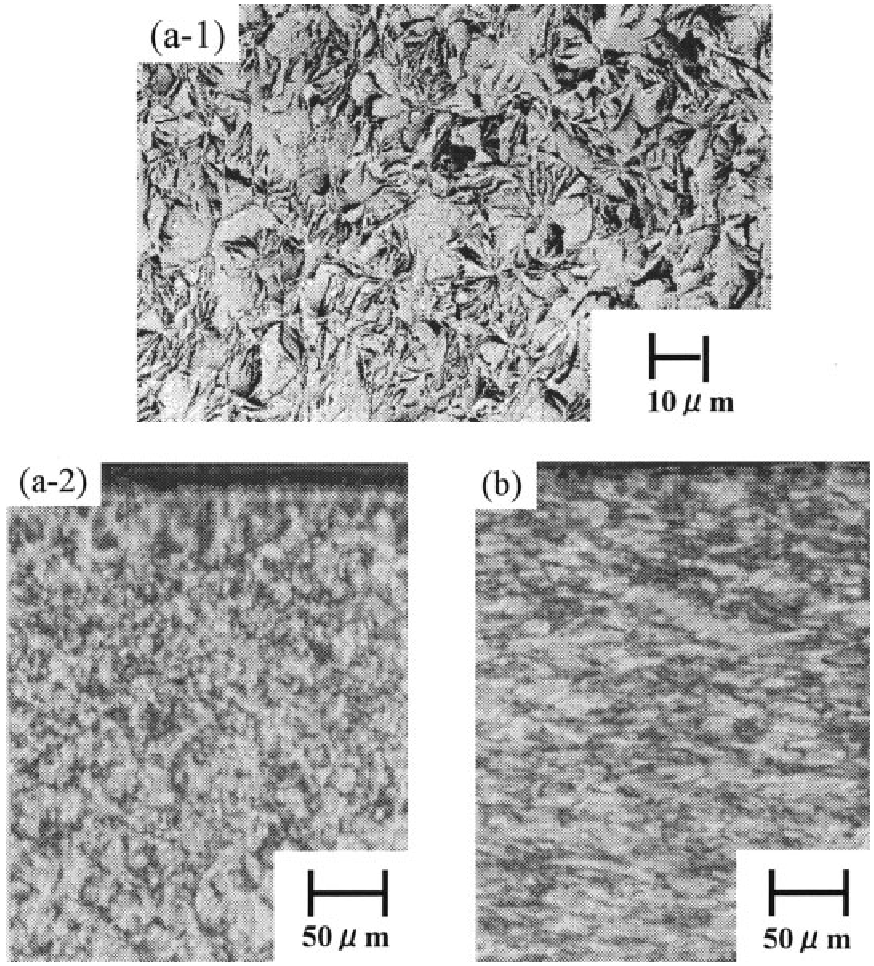

Figure 2 Photograph by SEM and polarizing microscope (PM). (a-1) SEM and (a-2) PM are before press and (b)PM is after press drawing.

size [meq]100 μm can be prepared under special conditions.[8]

The structural change of the POM crystal after the press drawing was observed by SEM and a polarizing microscope. The results are shown in Figure 2 Spherical structures were observed by SEM before the press drawing, and the boundary of the black area and the mosaic in the upper region was observed on the surface of the films by the polarizing microscope.

The degree of crystallinity, the tensile modulus of elasticity, and the draw ratio of the film were measured and the relation is plotted in Figure 3. The degree of crystallinity decreased with increasing draw ratio and it dropped from 70% to 65%. However, the drop was not clear in the higher drawing region. On the other hand, the tensile modulus increased with increasing draw ratio and the magnitude was 4.5 GPa in the higher drawing region. Generally speaking, as the moduli of the crystalline and amorphous phases are different, the tensile strength is also proportional to the crystallinity. However, the two kinds of data, the tensile modulus of elasticity and the degree of crystallinity, were not simply proportional to the draw ratio. It was suggested that the structural change during the drawing was complicated.

Regarding the relation between the draw ratio and tensile elongation, the tensile elongation increases up to a draw ratio of about 1.7×1.7, but then sharply decreases with a peak of 1.7×1.7 as shown in Figure 4. This is similar to the decrease of crystallinity as observed in Figure 3.

Up to a draw ratio of 1.7×1.7, the crystallinity decreases together with the draw ratio, and at higher draw ratios, there is almost no change of crystallinity. From the results shown in Figure 3 alone, the variation of the draw ratio and crystallinity is not clear, but if the results shown in Figure 4 are also taken into consideration, it is evident that a structural change occurs at a draw ratio of 1.7×1.7.

If the draw ratio of 1.7×1.7 is exceeded, the orientation of the molecular chain has more effect, the decrease of crystallinity is suppressed and the film becomes more rigid, so the elongation decreases. On the other hand, up to 1.7 times, the effect of orientation

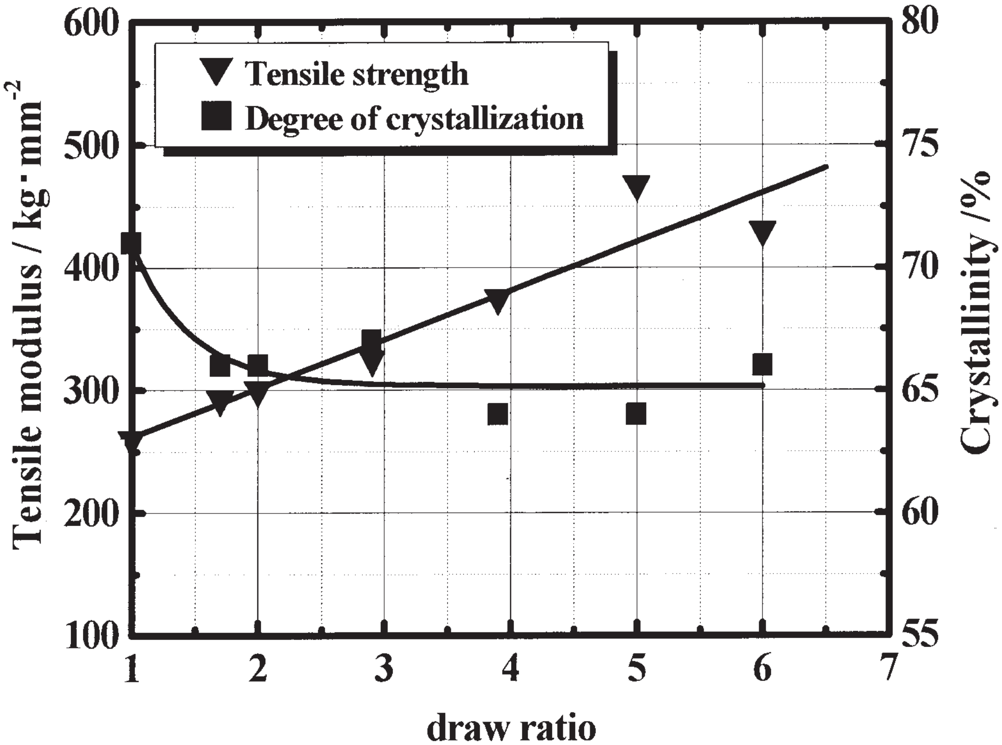

Figure 3 Tensile modulus of elasticity and degree of crystallinity as a function of the draw ratio.

is apparently small, so deterioration of the crystal structure due to the flattening of the crystals occurs, the crystallinity falls, and elongation increases.

Also, from Figure 4, when the draw ratio increases above 3.0 × 3.0, the tensile elongation falls more than that when the draw ratio is 1.0 × 1.0, suggesting that there are defects or minute voids in the structure of the material.

To analyze the deformation, the specimens, one of which was pressed by 2.0 × 2.0 times and another was

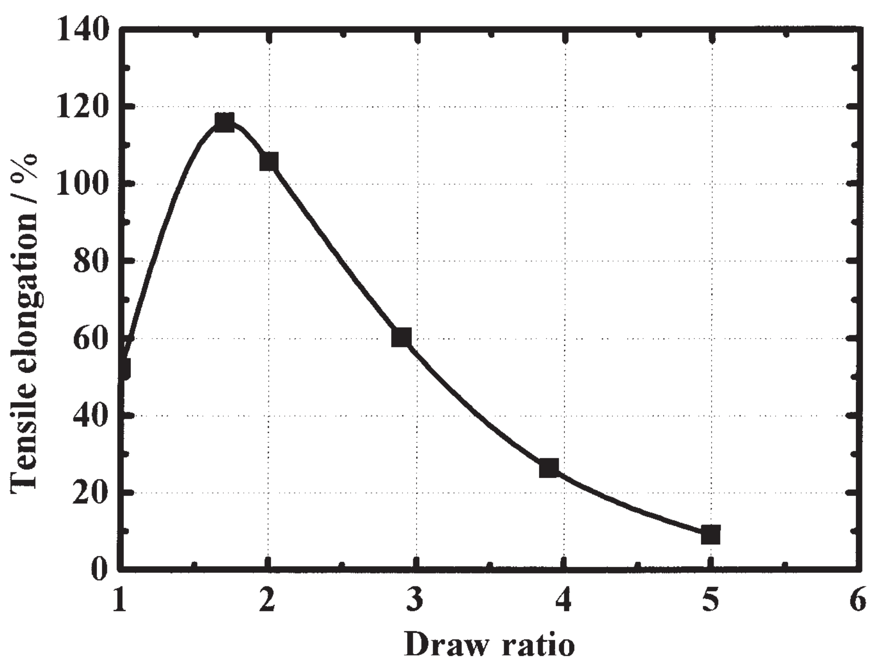

Figure 4 Rupture elongation as a function of the draw ratio.

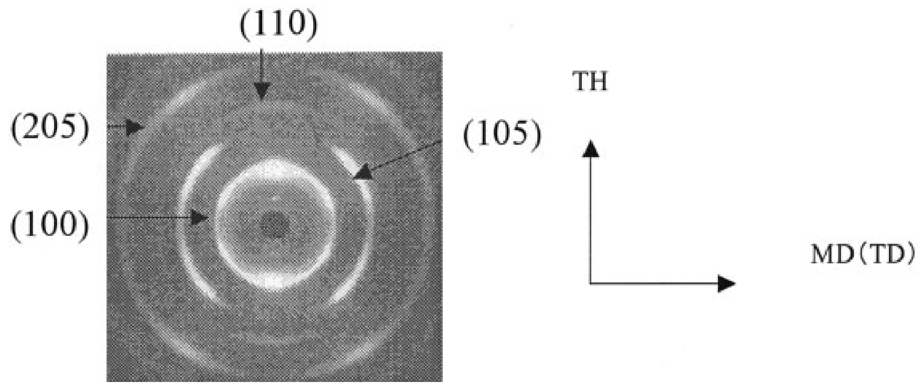

Figure 5 X-ray diffraction pattern of the specimen pressed by 4 × 4 times.

done by 4.0 × 4.0 times, were observed by X-ray diffraction. Figure 5 is the photograph of the X-ray diffraction pattern for MD or TD directions of the specimens pressed by 4.0 × 4.0 times. Since there is no directional anisotropy in the plane of film, the MD pattern and TD pattern are identical. The (100) diffraction was clear to form six-points image. It shows that the *c*-axis of the crystal was perpendicular to the press drawing direction.

The strength of the X-ray diffraction of (100) was plotted in Figure 6 by scanning X-ray (β-scan) parallel to (100). The strength at 90° of the 2.0 × 2.0 draw ratio was not so different from the other angles, which showed that the orientation was not so advanced. On the other hand, the strength of the 4.0 × 4.0 was very large, which showed that the orientation within the plane of the film was very strong.

Next, as it is considered that the crystallization was restrained by the mechanical holding pressure, the heat treatment was done for the specimen of 4.0 × 4.0 press drawing under the conditions shown in Figure 7. The degree of crystallinity slightly increased by the treatment at 150°C (5 min) and subsequently at 180°C (1 min), and the maximum value was 67% at 170 (5 min).

The reason why the crystallinity increases only up to about 67% because of heat treatment can be explained as follows. In press draw, the crystal structure first begins to break up and crystallinity decreases because of mechanical pressure. The draw ratio increases further and at a factor of about 4.0 × 4.0 part of the lamellar structure slips and becomes finer due to orientation. To increase crystallinity in this state, this disintegrated lamellar structure must be restored. For example, as in the two steps drawing of this study, heat elongation must be performed to rearrange the lamella and induce ordering/crystallization. Regarding the restoration of the lamella by heat treatment, this behavior has been observed also from small-angle X-ray measurements during the heat treatment of a rolled POM sheet 5. However, although simple heat treatment can restore the collapsed lamella to some extent, it cannot induce rearrangement, so it is 4%. It was thought that the increase in crystallinity has an upper limit of about 67%.

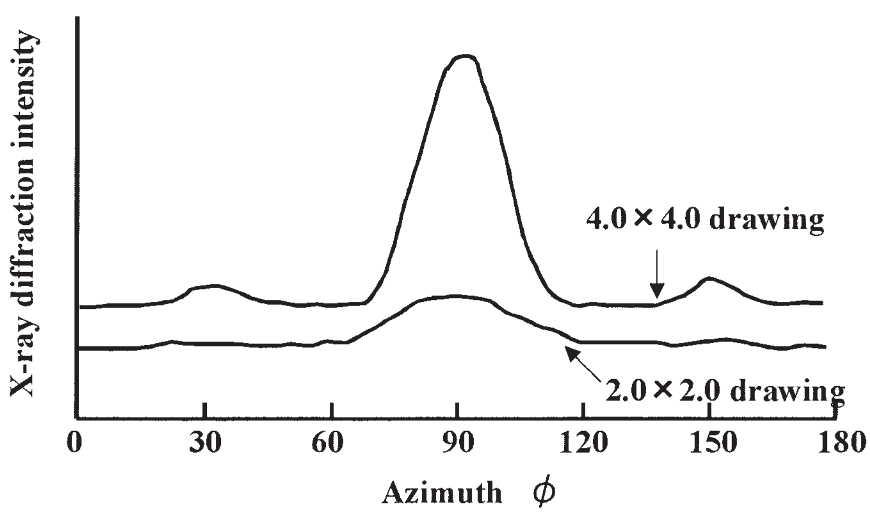

Figure 6 Crystal orientation of POM film by press drawing method.

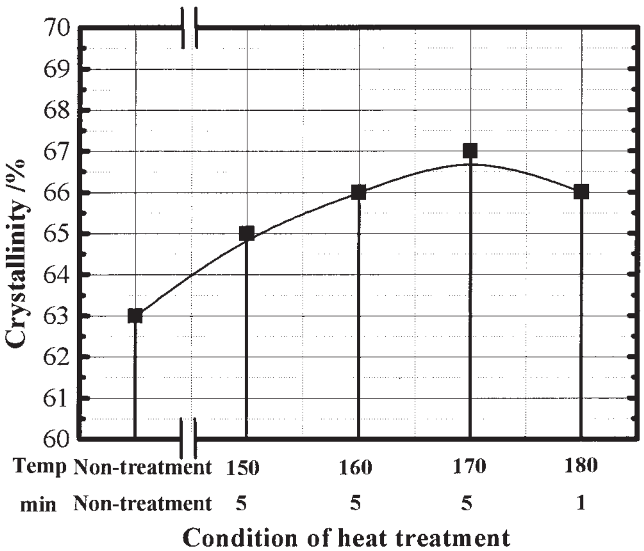

Figure 7 Degree of crystallinity under various treatments after press drawing (4.0 × 4.0).

Crystal structure after two-step drawing

Two-step drawing by press drawing and subsequent simultaneous biaxial drawing were studied. The press drawing film (draw ratio 2.0 × 2.0) was drawn by a 170°C simultaneous biaxial drawing machine (Stretcher). A high transparency film was obtained. Figure 8 shows the relation between the draw ratio and tensile modulus of elasticity by the two-step drawing compared with that of press drawing only. In the case of two-step drawing, the tensile modulus of elasticity increased up to 11 GPa when the draw ratio was 14 times.

Figure 9 shows the relation between the draw ratio and crystallinity of the film obtained by two-steps drawing that also includes simultaneous biaxial drawing following press drawing. The crystallinity after simultaneous biaxial drawing increases up to 76–80%, which is an increase of 5–9% from 71% for the raw film. This is probably due to the fact that the fine lamella are rearranged and ordered/crystallized by performing simultaneous biaxial drawing. It is considered that the tendency for the tensile modulus to be rather high after the two-step drawing incorporating simultaneous biaxial drawing is due to this difference in crystallinity.

However, the crystallinity after simultaneous biaxial drawing hardly depends on the draw ratio, and shows an effectively constant value (average 77%). The reason for this is as follows. Figure 10 is a SEM photograph after plasma etching of the surface of film obtained by simultaneous biaxial drawing, showing that the spherulitic texture that was present in the initial undrawn raw film is now completely absent. Since the parts rich in amorphous components are

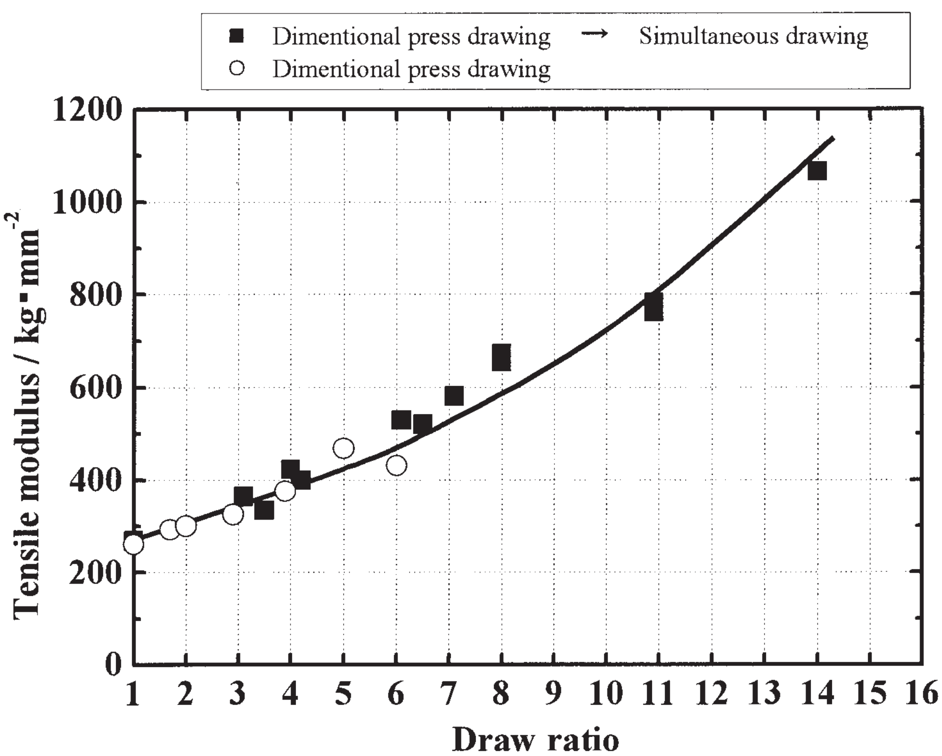

Figure 8 The relation between the draw ratio and tensile modulus of elasticity by the two-step drawing compared to that of press drawing only.

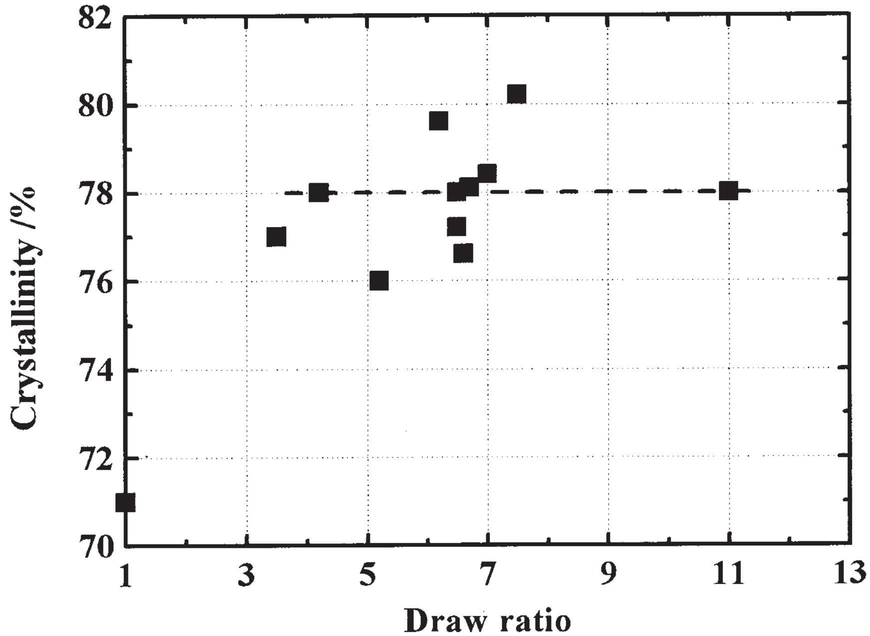

Figure 9 Crystallinity *vs.* draw ratio for the films obtained by two-step drawing, which performs simultaneous biaxial drawing following press drawing.

easily destroyed by plasma etching, it appears that the black parts in the photograph are parts rich in amorphous components. Thus, the lamella of the crystalline components of the film after drawing are finely broken up because of the drawing, and are surrounded by amorphous components.

Through the press drawing and subsequent simultaneous biaxial drawing, the lamellar structure that formed the original spherulitic morphology is broken up and finely divided by repeated slippage so that the orientation in the plane of the film becomes more ordered. When slippage occurs because of the drawing, amorphous components are newly formed. Even if the draw ratio increases, amorphous components are still newly formed so that although the lamella becomes finer and their orientation becomes more ordered, the crystallinity does not increase above a certain level. However, since the orientations of the fine lamella become stronger, the tensile modulus increases because of the orientation effect.

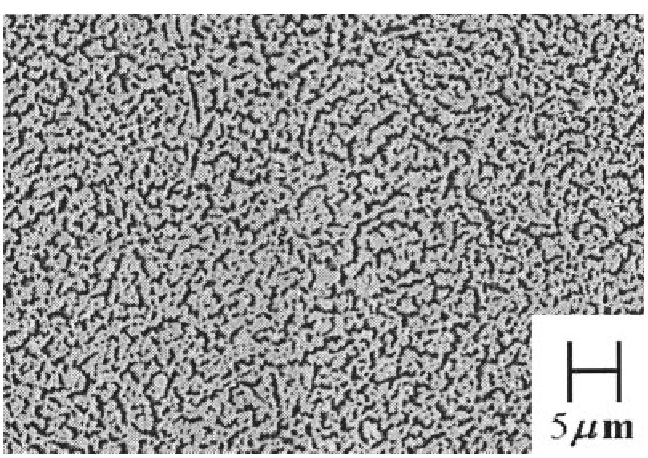

Figure 10 SEM photograph after plasma etching of the surface of film obtained by simultaneous biaxial drawing.

The reason why the tensile modulus of the biaxial drawn film of this study is much lower than the crystalline elastic modulus found by Sakurada et al.[7] or the mono-axial drawing material obtained by Nakagawa et al.,[8] is thought to be that although there is a difference between mono-axial drawing and biaxial drawing, the effect of the amorphous part surrounding this crystalline part is extremely large.

Figure 11 shows the X-ray diffraction photograph after two-step drawing combining press drawing with simultaneous biaxial drawing (draw ratio 11.0×11.0). Since there is no directional anisotropy in the plane of the film, the MD pattern and the TD pattern are identical. As can be seen from this photograph, the diffraction pattern was identical after press drawing. The (100) diffraction forms a six-point image, and the (100) reflection on the MD axis is strong. This shows that there is a structure with a definite planar orientation wherein the *c*-axis of the crystal is oriented perpendicular to the press direction, and the (100) plane is oriented parallel to the plane of the film.

From the aforesaid X-ray diffraction analysis, schematically representing the crystal orientation state of a POM biaxial drawn film, an identical orientation state is obtained after press drawing or subsequent simultaneous biaxial drawing, as shown in Figure 12.

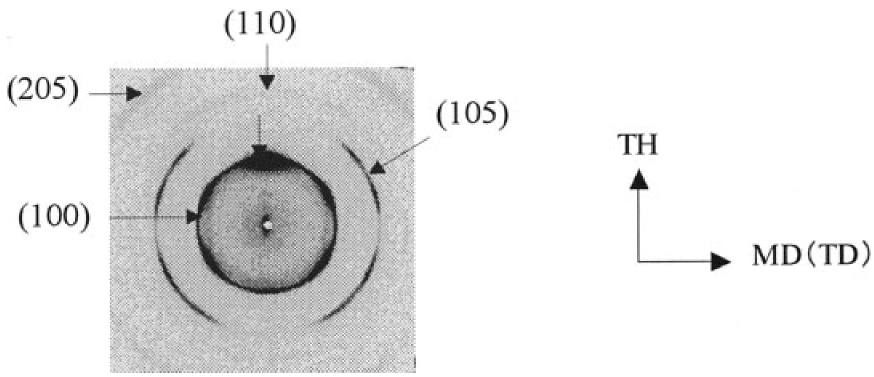

Figure 11 The X-ray diffraction photograph after two-step drawing.

The crystal structure of POM is basically spherulite, and the size of ordinary spherulite is 10–50 μm. It is known that this can be changed into a structure where the spherulite is finely divided by special methods, but attempts to make changes to the crystallinity or spherulite morphology by the usual methods have been unsuccessful. Figure 13 shows the unit structure of the POM crystal and the lamellar structure. The POM crystals belong to the hexagonal system, the minimum repeating unit (fiber period) consisting of nine CH_2O structural units inverted five times in a spiral. The fiber period is 17.3 Å, the spiral radius of the carbon atoms is 0.69 Å and the spiral radius of the oxygen atoms is 0.67 Å. This polymer forms a lamella structure like a hairpin that is bent backwards, having a thickness of approximately 100 A. This lamella grows out in the radial direction with a fixed period from the crystal nucleus while twisting to form the spherulite structure.

Thus, the POM crystal has anisotropy, and according to the experimental results of Sakurada et al. shown in Table I, the lattice elastic modulus in the direction of the molecular chain is 54 GPa, but in the perpendicular direction it is 8 GPa. According to Nakagawa et al., a superdrawing material of POM is formed wherein the crystals are actually oriented along the *c*-axis of POM, and the tensile modulus is of the order of 60 GPa. From this fact, it might be expected that if the crystal axes of POM were aligned, the tensile modulus of the material in this direction could be significantly increased.

It appears that in a molded film, the tensile modulus can be increased by drawing it to increase its orientation. Various methods have already been attempted to draw the POM in biaxial directions. For example, attempts to reduce the crystallinity of the film has been made prior to drawing so as to facilitate drawing by (1) increasing the molecular weight, (2) decreasing the crystallization rate, and (3) preventing crystallization by rapid cooling. In (1), crystallization is inhibited and molecular weight is increased, which increases entanglements so that the material can withstand a high drawing stress. In general, in polymer materials, when the molecular weight decreases, the strength decreases, but in the case of POM, the crystallinity is high so the fracture toughness decreases considerably with the decrease of molecular weight.[9] In (2), the crystallization rate is retarded and the crystallinity is decreased by adding a small amount of an additive (crystallization retarding agent) to the extent that it does not affect physical properties much. In (3), the aim is to obtain high elongation by decreasing crystallization, by rapid cooling during casting. By employing these methods, the crystallinity can be decreased to some extent, but in the case of POM, since the crystallinity does not vary so much, an improvement of drawing properties is not obtained.

When it still has a high crystallinity without reducing the crystallinity of raw film prior to drawing, it was thought that the effective method would be to finely divide the material by adding crystalline nuclear material to the crystal structure or to the spherulite structure in the case of POM, thereby increasing the proportion of tie molecules between crystals so as to withstand a high drawing stress. But in practice there was not much improvement of drawing properties.

For POM spherulite, studies are also in progress to try to change the lamellar structure by methods such

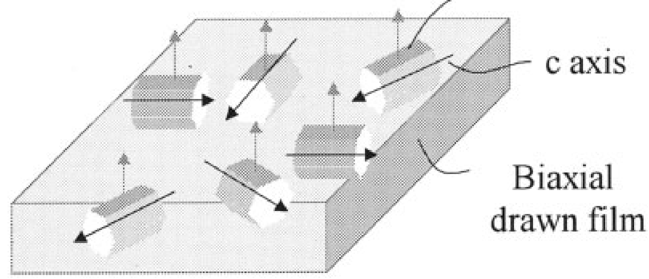

Figure 12 Schematic representation of the crystal orientation state of the POM biaxial drawn film.

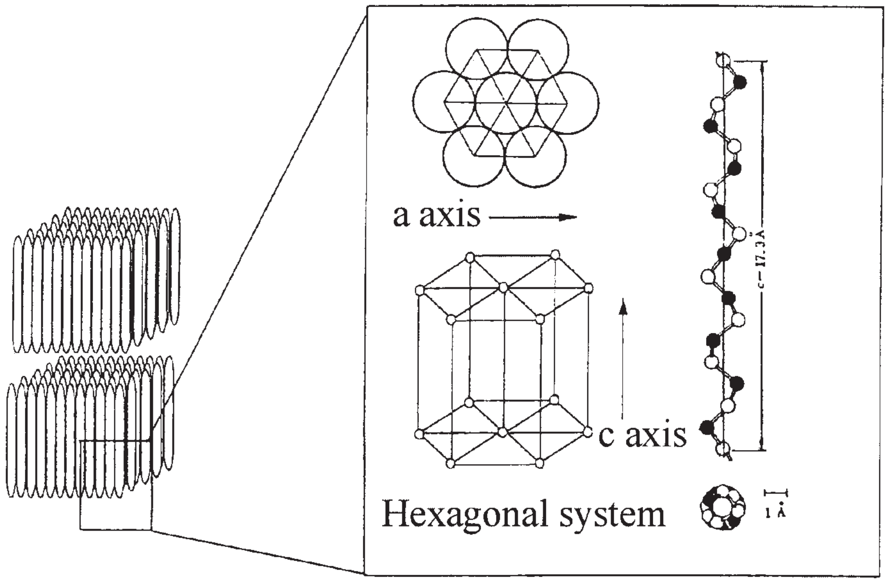

Figure 13 Unit structure of POM and lamella in POM.

as chemical etching.[10] In another method, rolling is performed in the first step[6] and drawing is performed afterwards,[11] but if drawing is performed using a roller, drawing can basically be obtained only along machine direction, and if the draw ratio increases, fracture may occur because of the high stress. In the biaxial drawing method using a press according to the present study, by orienting the crystals while mechanically applying high pressure, the material can be uniformly oriented in two directions while inhibiting fractures by applying the high pressure uniformly, but it is difficult to maintain a high crystallinity after drawing.

In general, it is said that to draw POM, in the low drawing region of 1–3 times, the lamellar are inclined at a certain angle, in the medium drawing region of 3–6 times, the lamella orientation is more pronounced, while in the high drawing region of 6 times and above, the lamella slip in the direction of the molecular chain so that the lamellar become more finely divided and crystal orientation becomes more ordered.

POM biaxial high drawn films have been developed as universal film materials, which make use of the excellent properties of the film itself, and the fine porous films obtained after drawing have many different applications. A morphology is also being studied where a fine porous film is prepared by a step such as heat annealing after extrusion molding so as to form numerous fine pores during drawing.[12,13] Moreover, elastic modulus and other properties are recently being measured in extrusion molding studies carried out on micro-extrusion molding materials other than films.[14]

Hence, basic knowledge has been gained regarding films obtained by drawing POM, but the drawing and the structures obtained under various conditions or their properties are still not well understood. It also appears that compared with PET (polyethylene terephthalate) or PEN (polyethylene naphthalate), which are used as high tensile modulus films (Table II), the faster crystallization rate and higher crystallinity of POM make film formation difficult.[15]

CONCLUSIONS

The physical structure of oriented polyoxymethylene (POM) drawn in two steps by press drawing and the subsequent simultaneous biaxial drawing was studied, and the degree of crystallinity, the orientation, and the tensile modulus and their dependence on draw ratio were analyzed. The results are as follows:

TABLE I
Lattice Elastic Modulus of Crystals in POM

	Lattice plane employed for measurement	Lattice elastic modulus (kg/mm^2)
Direction of the molecular chain	(009)	5400 (54 GPa)
Perpendicular direction of the molecular chain	(1010)	800 (8 GPa)

TABLE II
Comparison of the Characteristics of POM, PET, and PEN

Property	POM	PET	PEN
Glass transition temperature (°C)	−80	70	113
Melting point (°C)	178	262	273
Relative crystallized rate	<<1	1	7.5
Degree of crystallinity (%)	65–90	40–60	40–60
Density			
Crystal	1.506	1.455	1.407
Amorphous	1.25	1.331	1.325

1. By the press drawing method, the draw ratio reached 6.0 and the tensile modulus was 4.5 GPa, and the degree of crystallinity decreased from 70% to 65%.

2. By the press drawing method, the tensile elongation increased up to a draw ratio of about 1.7 × 1.7, but then sharply decreased with a peak of 1.7 × 1.7. Up to a draw ratio of 1.7 × 1.7, the crystallinity decreased together with the draw ratio, and at higher draw ratios, there was almost no change in crystallinity.

3. By the two-steps drawing of press drawing and subsequent simultaneous biaxial drawing, the tensile modulus reached 11 GPa when the draw ratio was by 14 times, and the degree of crystallinity increased from 71% to 76−80%, but it did not depend on the draw ratio, and showed effectively constant value (average 77%).

4. The SEM photograph after plasma etching of the surface of film obtained by the two-step drawing showed that the spherulite, which was present in the initial film, was completely absent, and that the lamella of the crystalline components were finely broken up because of the drawing, and were surrounded by amorphous components.

5. The X-ray diffraction pattern after the two-step drawing was identical after the press drawing. The (100) diffraction showed that the *c*-axis of the crystal was oriented perpendicular to the press direction, and the (100) plane was oriented parallel to the plane of the film.

The authors extend their sincere appreciation to Professor Takeda for his kind advice and the members of Asahi Chemicals and Nagoya University who assisted this research.

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