Young Modulus and Degree of Crystallization of Highly-Elongated Polyoxymethylene

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ABSTRACT: The physical structure of polyoxymethylene (POM) drawn into two steps by a press and a simultaneous biaxial drawing machine was studied and the drawing dependency on the degree of the crystallization, the orientation, and the modulus were analyzed. The stretching ratio by the press reached 6.0 and the tensile modulus of elasticity increased from 2.5 to 4.5 GPa. However, the degree of crystallization decreased slightly. The rupture elongation increased in the lower drawing region and it peaked when the drawing ratio was 1.7. The film stretched by 2 times was drawn by the biaxial drawing machine. The high tensile modulus of elasticity was obtained and the maximum value was 11.5 GPa at 14 times of the drawing ratio. The lamella structure of POM was supposed to loosen and become oriented to the drawing axis ambiguously by the first drawing. The lamella was highly oriented by the second stretching procedure. The tensile strength and the elongation as well as the modulus were analyzed as a function of the degree of the stretching and the crystallization. J Appl Polym Sci 101: 1223–1227, 2006

Key words: polyoxymethylene; films; elongation; orientation; crystallization

INTRODUCTION

Polyoxymethylene (POM) is one of the five major engineering plastics and the annual production rate is about 600,000 tons worldwide and 83,000 tons in Japan. It is mainly applied for mechanical parts and shows excellent performance against wear. It is a useful material in the plastic industry for it is easily prepared from formaldehyde and has a simple chemical structure in addition to the excellent characteristics. Many kinds of parts made of POM have been used for various purposes, but few applications of its film have been known. As the film has interesting performances, its usefulness is expected to become recognized.

The drawing of the sheet is indispensable to give the film excellent characteristics. Gezovich and Geil studied the drawing in their series of the processing research.[1] Clark and coworkers and Bahadur also reported the result in the region of low degree of the drawing.[2,3]

The results obtained from the studies on the drawing of POM in the region of middle and high degrees of the drawings and the relation between its structure and characteristics, in particular, the continuous drawings by a biaxial drawing press and a simultaneous drawing method are reported in this article.

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EXPERIMENTAL

Materials used

The POM used in this study was a linear homo-polymer manufactured by Asahi KASEI Chemicals (grade no. TENAC 3010). The molecular weight was 60,000 (Mn). To obtain a sheet of 0.70 mm in thickness and 150 mm in width, the POM was melted at 200°C to cast into 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 for the first step. The specifications of the press were (1) the size of the press board was 400 × 400 mm^2, (2) the temperature range was from 25 to 250°C, and (3) the maximum pressure was 50 tons by manually operated mechanism.

Five sheets and boards, namely (1) a electroplated steel plate, (2) PMMA board (10 mm thickness), (3) nondrawing polypropylene, (4) POM sheet, and (5) a

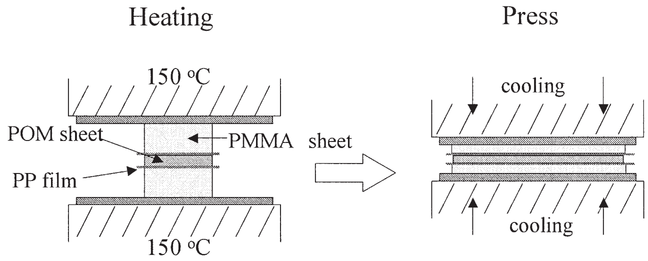

Figure 1 Outline of press method.

electroplated steel plate, were put between two press boards as shown in Figure 1.

After the temperature was elevated from 25 to 150°C, it was maintained for 10 min. The POM sheet was quickly moved to the cooling presser and drawn to the designed degree.[4,5] 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 strength. The two-steps drawing procedure is depicted in Figure 2. The temperature at the second drawing was set at 170°C.

Measurement of drawing film

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

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

where d_c is the density of the crystallized site (1.506 g/mL) and d_a is the amorphous site (1.250 g/mL). A polarizing microscope equipped with a sorthogonal

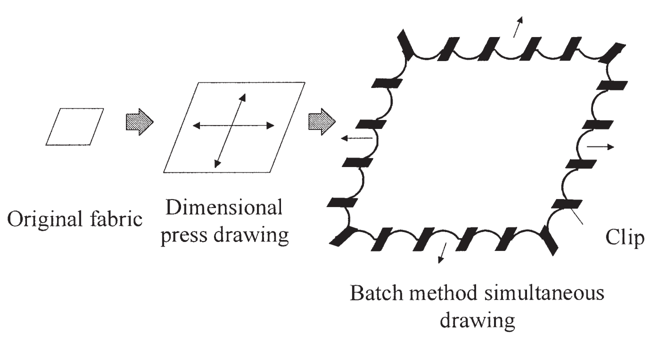

Figure 2 The two-steps drawing procedure.

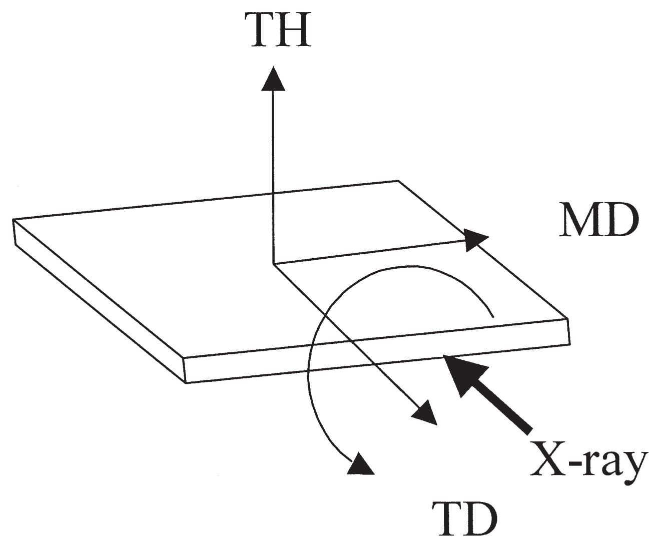

Figure 3 Incident direction of X-ray and three directions (TH, TD, and MD).

polarizer was used for the visual observation of the crystal structure.

The tensile modulus of elasticity was calculated from the data of a tensile test. The tensile strength and the elongation of the specimen (100 mm length and 10 mm width) were measured by a tensile tester in the atmosphere (temp. = 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 applied for observing the crystal structure. A XD-3A diffraction apparatus manufactured by Shimazu Co. was used. The source of X-ray was the filtered Cu Kα line of Ni and the strength was 30 kV–28 mA. The monochromator for the WAXD photo was used.[6]

The angles of the incidence were the direction of TH, TD, and MD as depicted in Figure 3 to photograph 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 the POM (100) (2θ = 22–23.5°) and subsequently the plate was rotated by 4° a minute.

RESULTS AND DISCUSSION

Visual observation of crystal structure after the press method

The structural change of the POM crystal after the press drawing method was observed by a polarizing microscope. The results are shown in Figure 4, in which the boundary of the black area and the mosaic in the upper region is the surface of the films.

The degree of the crystallization is from 60 to 80% and the shape is spherical. The size is 10–50 μm and

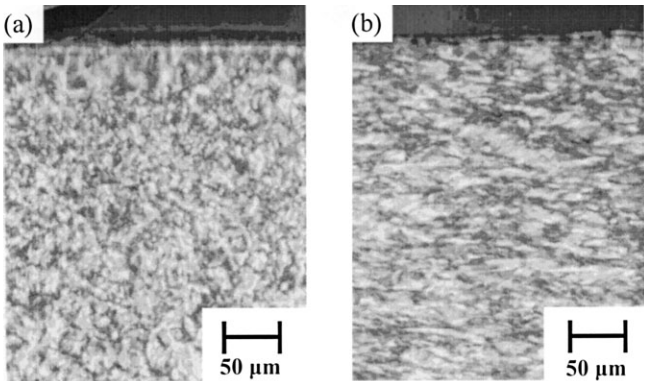

Figure 4 Crystal condition before (left) and after (right) drawing.

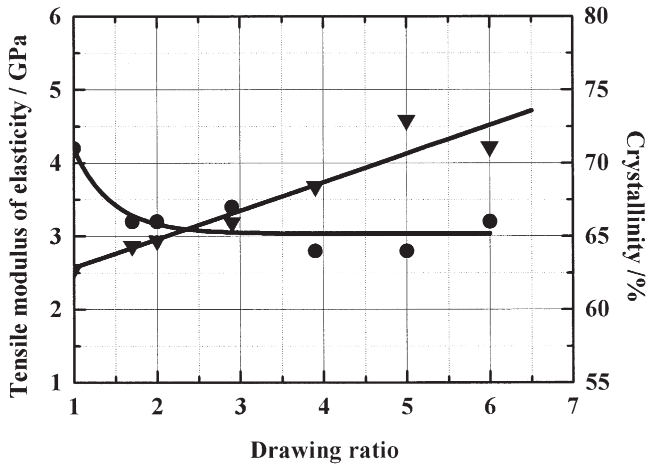

Figure 6 Tensile modulus of elasticity and degree of crystallization as a function of drawing rate.

the larger crystal whose size is 100 μm or more can be prepared under the special condition.[7]

The small spherical crystals of 20–30 μm were observed and were homogeneous in all directions before drawing (left in Fig. 4) and the direction was observed after the drawing as shown in the right photo of Figure 4.

To confirm the uniformity of the drawing, the check pattern was painted on the surface of the specimen and observed before and after the press. The drawing ratio of two directions was the same as shown in Figure 5.

Tensile modulus of elasticity and elongation (press method)

The degree of the crystallization and the tensile modulus of elasticity to the drawing ratio of the film were measured and the relation was plotted in Figure 6. The degree of the crystallization decreased with increasing drawing 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 of elasticity increased with increasing drawing ratio and the magnitude was 4.5 GPa in the higher drawing region. Generally speaking, as the modulus of the crystal and the amorphous sites were different, the tensile strength is also proportional to the crystallinity.

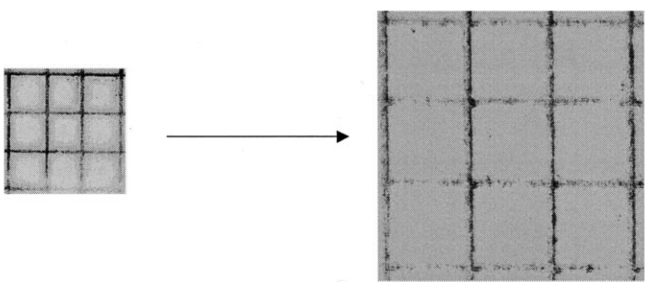

Figure 5 Check pattern before and after press drawing.

However, the two kinds of data, the tensile modulus of elasticity and the degree of the crystallization, were not simply proportional to the drawing ratio. It suggested that the structural change during the drawing was complicated.

Figure 7 shows the tensile elongation as a function of the drawing ratio. The elongation increased initially and decreased rapidly after it hit the peak when the ratio was 1.7. It is considered to show the relation between the degree of the crystallization and the drawing ratio.

The degree decreased by 1.7 of the drawing ratio and was constant in the higher region (Fig. 7). The data suggested the microscopic structural change in the POM. First, the spherical crystal changed to a somewhat flat shape and it caused the structural disorder in the lower region of the drawing ratio. The decrease of the degree of crystallization and higher

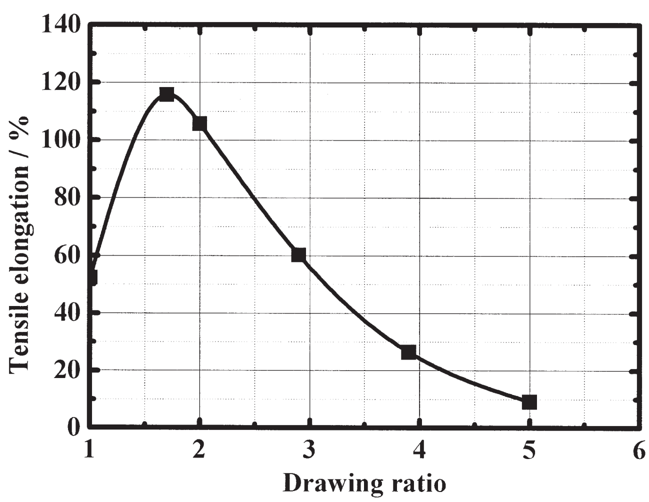

Figure 7 Tensile elongation as a function of the drawing rate.

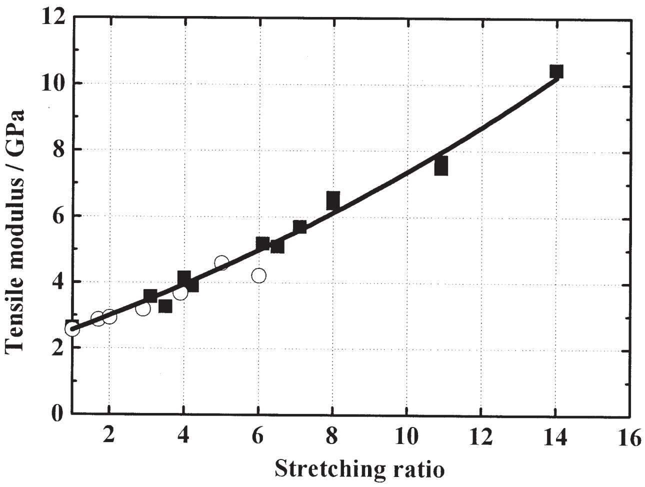

Figure 8 Tensile modulus of elasticity of the two-steps drawing as a function of the drawing ratio.

elongation were due to the change. In the higher drawing ratio, the orientation of the lamella suppressed the decrease of the crystallinity. It caused the decrease of the elongation.

The elongation when the drawing ratio was 3.0 or more was smaller than that of the original specimen. It is considered to be due to a defect such as a microscopic void generated in the drawn POM.

The two-steps drawing by press and simultaneous biaxial drawings

Making use of the results of the press drawing, the specimen drawn by 2 times was drawn by the simultaneous biaxial stretcher because the crystal in the POM loosened by a small drawing by the press. The maximum drawing ratio was 14 and the tensile modulus of elasticity hit 11 GPa. This magnitude is much higher than that observed for the stretched specimen by an injection molding method.[8] The film was transparent and the crystallinity was 76–80%. The tensile modulus of elasticity was plotted to the drawing ratio in Figure 8. The result of the press drawing was also plotted in the same figure to be compared with the two-step methods. The tensile modulus of elasticity increased monotonously and the slope of the two-step method was a little higher than that of the press. The tensile strength and the tensile elongation were also plotted in Figure 9.

The strength increased and the elongation decreased with increasing drawing ratio. The strength sharply dropped by 14 times of the ratio and the elongation decreased. It showed the defect in the POM at the higher drawing region. If the microscopic heterogeneous structure or the impurity can be extricated (removed), a higher strength should be obtained.

The microscopic particle of the POM crystal is generally recognized to be columnar (lamella) and the axis inclined under the lower drawing condition. The crystals are oriented to the drawing direction in the middle drawing and finally the lamella slides to the drawing direction to orient in the same direction. The plural lamellas exist apart from each other and the ligament space becomes a void. So, a large number of voids are generated and the film has been applied for the porous membrane.[9]

Polyethyleneterephthalate (PET) and polyethylenenaphthalate (PEN) are well known to be easily obtained highly drawn film.[10] The rate and the degree of POM crystallization are much higher than those of PET and PEN. It is one of the reasons that the highly drawn film can be prepared in the case of POM.

However, the modulus of the crystal is different by the direction of the crystal, as shown in Table I. That of the axis direction is about 54 GPa, whereas that of the vertical direction is about 8 GPa.[11] Actually, Nakagawa and coworkers obtained the specimen whose

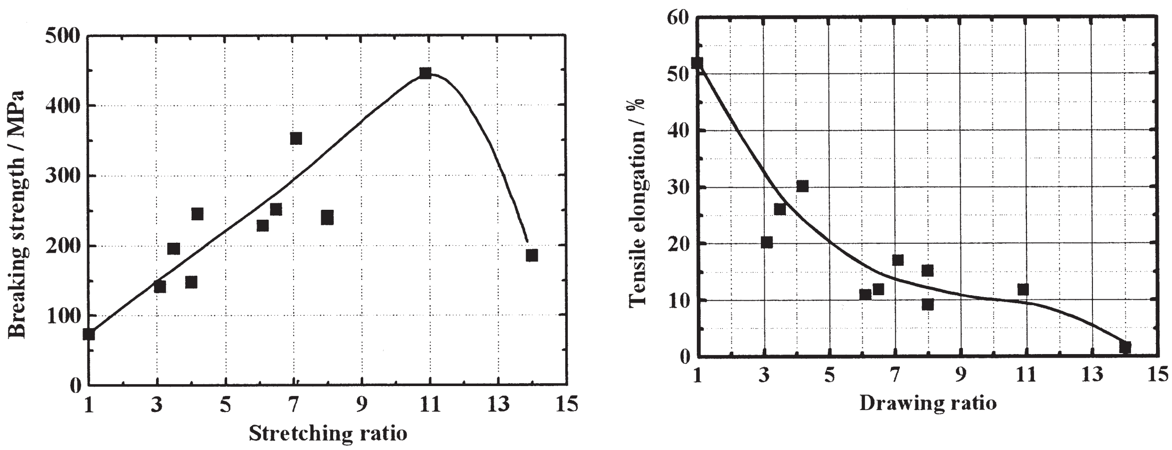

Figure 9 Tensile strength (left) and elongation (right) of the two-steps drawing.

TABLE I
Theoretical Modulus of Crystals in POM

	Crystal face	Crystal modulus (GPa)
Direction of axis	−9	54
Vertical direction	−1010	8

tensile modulus of elasticity was 60 GPa though it was stretched in a mono-axial direction.[12]

There have been many attempts to obtain the specimen whose tensile modulus of elasticity is high enough by a biaxial drawing. Enhancing the molecular weight, decreasing the rate of the crystallinity and rapid cooling are some examples. As the strength of polymeric material increases with increasing molecular weight, enhancing the molecular weight is considered to be one of the more promising methods. However, the tendency of POM is different because of the high degree of crystallization.[13]

The aim of the second and the third methods is to prevent the formation of the crystal. However, the degree is hardly affected by the conditions, such as temperature and time.

A more sophisticated method in which the spherical crystal in the POM film is etched by chemicals and deformed into another shape is attempted.[14] The two-steps drawing was studied where the POM film was first stretched by a drawing role and the second drawing was done successively.[15,16] Highly drawn POM was not prepared by these methods.

The reason why 11 GPa of the tensile modulus of elasticity was observed in this study can be considered as follows.

The size of the crystal is about 10–50 μm and the size and the shape cannot be changed by the mechanical procedure such as molding and drawing under various temperatures and speeds. On the other hand, the crystals form a lamella structure by bending and holding the polymer chain and each lamella is bonded with polymer chains. So, the lamella can move slightly and change the mutual position in the lower drawing region by the press method in this study. The crystal structure of the POM comes loose and the directions of the lamella become regular to be re-oriented by the second drawing procedure.

CONCLUSIONS

POM is known as a polymer whose rate and degree of crystallization are high and recognized as highly oriented film. The condition and the properties of the highly drawing film of POM were studied. The results are as follows:

1. Drawing ratio of 6 × 6 times could be obtained by the press method.
2. The spherical crystals oriented in a vertical direction against the press direction.
3. The degree of crystallization decreased from 70 to 65%, but the decrease was not observed in the higher drawing region.
4. The elongation increased at 1.7 times of the drawing and it dropped in the higher drawing region.
5. The tensile modulus of elasticity increased from 2.5 to 4.5 GPa in proportion to the drawing ratio.
6. 11 GPa of the tensile modulus of elasticity was observed by drawing the press and the simultaneous biaxial methods and the drawing ratio was 14 times.
7. The crystallinity of the highly drawn film was 78–80% and the film was transparent.
8. The degree of the crystallization did not depend on the drawing ratio and the average was 77.9%.

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