Production of ultrahigh modulus polyoxymethylene by drawing under dielectric heating

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A tensile drawing process under dielectric heating has been developed for polyoxymethylene. The influence of ambient temperature, electric field strength, and strain rate on the maximum draw ratio and the tensile modulus has been examined. Tubes possessing tensile moduli up to 63GPa were produced by the new drawing technique. It is speculated that the achievement of such ultrahigh moduli is due to the fact that the stress by drawing is used effectively to orient the molecular chains in the noncrystalline regions and at defect regions within the crystal lamellae. This is because these regions are heated to higher temperatures than the crystalline regions during dielectric heating.

(Keywords: production; polyoxymethylene; drawing; dielectric heating)

INTRODUCTION

Recently, techniques for the production of ultrahigh-modulus oriented polymers have been investigated by many workers[1]. Polyoxymethylene (POM) is one of the most highly investigated polymers for the production of ultrahigh modulus polymers. An ultra-oriented POM fibre, which has a tensile modulus of 35 GPa (draw ratio of 20), was produced by a two-stage drawing process[2]. Brew and Ward[3] obtained a tensile modulus of 39.5 GPa by drawing a dumb-bell shaped POM sample up to a draw ratio of 23 using a tensile testing machine. Oriented POM rods with tensile moduli up to 25 GPa were produced at relatively low production rates by hydrostatic extrusion[4] and by die drawing[5].

We have already reported that ultrahigh-modulus POM rods and tubes can be produced by tensile drawing under dielectric heating[6].

In POM there are three dielectric absorptions, i.e., α, β and γ absorptions[7]. The α absorption is attributed to the translational motions of molecular chains along the chain axis in the crystalline regions and the absorption peak occurs at low frequencies near 10 Hz and at high temperatures near 140°C. The β absorption is due to main-chain micro-Brownian motions in the disordered interlamellar regions, i.e., the noncrystalline regions. The β peak occurs at high frequencies of 1 kHz to 1 MHz in the temperature range of 60° to 100°C. The γ absorption results from the local motions of molecular chains in the noncrystalline regions and at defect regions within the crystal lamellae. The γ peak occurs at high frequencies near 1 GHz. As the temperature rises, these absorptions are enhanced and transformed on the higher frequency side, and are fused together at the melting point of about 180°C. It is, therefore, difficult to excite a desired absorption at the vicinity of the melting point by applying an alternating current field. Below the melting point, however, the β and γ absorptions may be selectively excited to heat the noncrystalline regions and crystal defect regions, by applying an alternating current field with a high frequency such as 2.45 GHz (in the microwave region). On the other hand, the crystalline regions may be heated to a lesser extent because the α absorption cannot be excited by the applied microwave.

In this way, it is expected that the disordered regions such as the noncrystalline regions and the crystal defect regions are selectively heated more intensely than the crystalline regions by means of dielectric heating. Under tensile drawing with dielectric heating, therefore, the drawing stress acts effectively upon the disordered regions. This results in an effective amorphous orientation because the reduction in tensile modulus due to excessive heating of the crystalline regions can be suppressed.

In this paper, we will examine the effect of drawing under dielectric heating and also the influence of ambient temperature and electric field strength on the drawing behaviour (since the draw temperature cannot be measured during dielectric heating).

EXPERIMENTAL

Samples

The material used was a commercially available POM (Tenac 5010, Asahi Chemical Industry Co., Japan). The number average molecular weight was 37 000, the density 1.42 g cm^{-3}, and the melting point 179°C. Three types of samples were used for the drawing experiments: two rods of 1 mm and 2 mm in diameter and one tube with outer and inner diameter of 3 mm and 1 mm, respectively.

Drawing apparatus

Figure 1 shows the appartus for drawing under dielectric heating. The apparatus is comprised of a feed reel (2), a belt catapillar-type feeder (3), a dielectric heating apparatus (4), in which the sample is subjected to dielectric heating, a belt catapillar-type take-up machine (11), and a take-up reel (12). The dielectric heating apparatus (4) includes a microwave power source (5), a rectangular waveguide (6) for jointing, a circular waveguide (7) for

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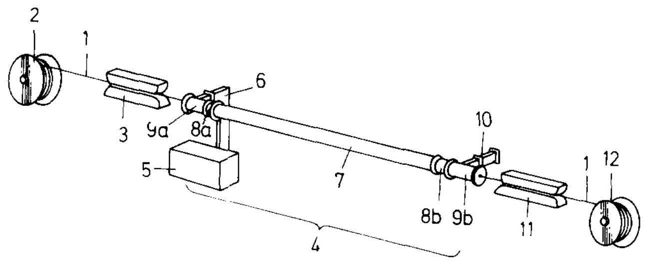

Figure 1 Apparatus for drawing under dielectric heating: (1) drawing sample, (2) feed reel, (3) caterpillar-type belt feeder, (4) dielectric heating apparatus, (5) microwave power source, (6) rectangular waveguide for jointing, (7) circular waveguide for dielectric heating, (8a, 8b, 9a and 9b) circular waveguides for matching, (10) dummy load, (11) belt caterpillar-type take-up machine, (12) take-up reel

dielectric heating, circular waveguides (8a), (8b) and (9a), (9b) for matching, and a dummy load (10). A continuous-wave magnetron (2.45 GHz, 1.5 kW max) was used as the microwave power source (5), (9). The circular waveguide (7) was made of copper. The inner diameter was 95.6 mm and the length was 0.5 m or 3 m. The furnace length refers to this length. The ambient temperature of the inside of the circular waveguide (7) can be controlled by electric heaters mounted around the circular waveguide. The inner diameter of the circular waveguides (8a) and (8b) for matching is somewhat larger than that of the waveguide (7), and the inner diameter of the circular waveguides (9a) and (9b) is also somewhat larger than that of the circular waveguides (8a) and (8b). The microwave generated from the microwave power source is effectively guided in the TM_{01} mode through the rectangular waveguide (6) and the circular waveguides (9a) and (8a) to the circular waveguide (7) for dielectric heating without being reflected. The excess microwave power is guided through the circular waveguides (8a) and (9b) for matching to the dummy load 10. The ends of the waveguides (9a) and (9b) are closed by lid plates, and a hole is provided at the centre of each lid plate to pass the sample through.

Tensile measurements

The tensile modulus measurements of the drawn samples were performed at room temperature on a tensile testing machine. The sample guage length was 150 mm and the crosshead speed was 5 mm min^{-1}. The initial strain rate was 0.033 min^{-1}. The strain was measured using an extensometer with a mark distance of 50 mm. The tensile modulus was determined from the tangent to the stress–strain curve at 0.1% strain. The cross-sectional areas of the samples were determined by weighing a length of sample in a microbalance and determining the sample density in a toluene/carbon tetrachloride density gradient column. The densities were in the range of 1.41–1.44 g cm^{-3}.

RESULTS AND DISCUSSION

Effect of drawing under dielectric heating

The effect of drawing under dielectric heating was examined for a POM rod with a diameter of 1 mm (using the circular waveguide (7) of *Figure 1*) for dielectric heating with a length of 0.5 m (furnace length of 0.5 m). At first, both the feeder and take-up machine speeds were set at 1 m min^{-1}. But the feed speed was gradually reduced to raise the draw ratio. When the ambient temperature of the inside of the circular waveguide was equal to room temperature, no necking occurred at dielectric heating with a maximum output of 1.5 kW (electric field strength of 520 V cm^{-1}). The ambient temperature was, therefore, raised. Since the electric field strength in the dielectric heating furnace could not be measured directly, it was calculated from the output of the microwave power source using the following equation which is generally applicable in the case of a copper-made circular waveguide:

$$E = 100P^{1/2}\left\{0.265\left(\frac{2.61R}{\lambda}\right)^2\frac{R^2}{240}\left[1-\left(\frac{\lambda}{2.61R}\right)^2\right]^{1/2}\right\}^{1/2}$$
$$= 13.5P^{1/2}$$

where E is the electric field strength ($V\,cm^{-1}$), P the output (W), R the radius (m) of the circular waveguide and λ the wavelength (m).

Figure 2 shows that the maximum draw ratio obtainable at each ambient temperature increases from 19–30 with increasing ambient temperature from 140°–158°C under dielectric heating. The highest tensile modulus of 36 GPa was attained at an ambient temperature of 149°C. Above this temperature the tensile modulus decreases with increasing ambient temperature. For comparison, the drawing experiments were undertaken in the same range of the ambient temperature with no dielectric heating. The maximum draw ratio increases from 11–15 with increasing ambient temperature from 141°–158°C. The highest tensile modulus was 20 GPa at the same ambient temperature of 149°C. In this way, the higher draw ratio and the higher tensile modulus are obtainable by drawing under dielectric heating at appropriate high ambient temperatures.

In order to produce the high modulus POM at higher speeds, the furnace length was extended from 0.5 m to 3 m. The effect of drawing under dielectric heating has been also examined for a POM rod with a diameter of 2 mm. The take-up speed was fixed at 2 m min^{-1} and the feed speed was gradually reduced to raise the draw ratio. The drawing experiments were made at ambient temperatures of 125°–146°C under electric field strengths of 320 V cm^{-1} (output of 0.57 kW) and 410 V cm^{-1} (0.95 kW).

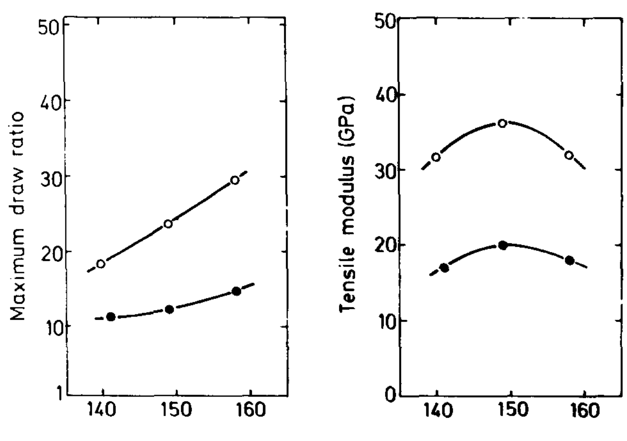

Figure 2 Maximum draw ratio and tensile modulus *versus* ambient temperature. Rod diameter 1 mm; furnace length 0.5m; take-up speed 1 m min^{-1}; electric field strength (○) 520 V cm^{-1} (1.5 kW), (●) 0 V cm^{-1}

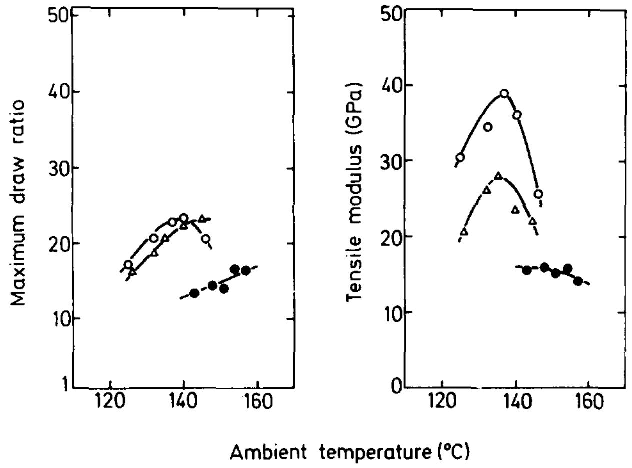

Figure 3 Maximum draw ratio and tensile modulus *versus* ambient temperature. Rod diameter 2 mm; furnace length 3 m; take-up speed 2 m min^{-1}; electric field strength (○) 410 V cm^{-1} (0.95 kW), (△) 320 V cm^{-1} (0.57 kW), (●) 0 V cm^{-1}

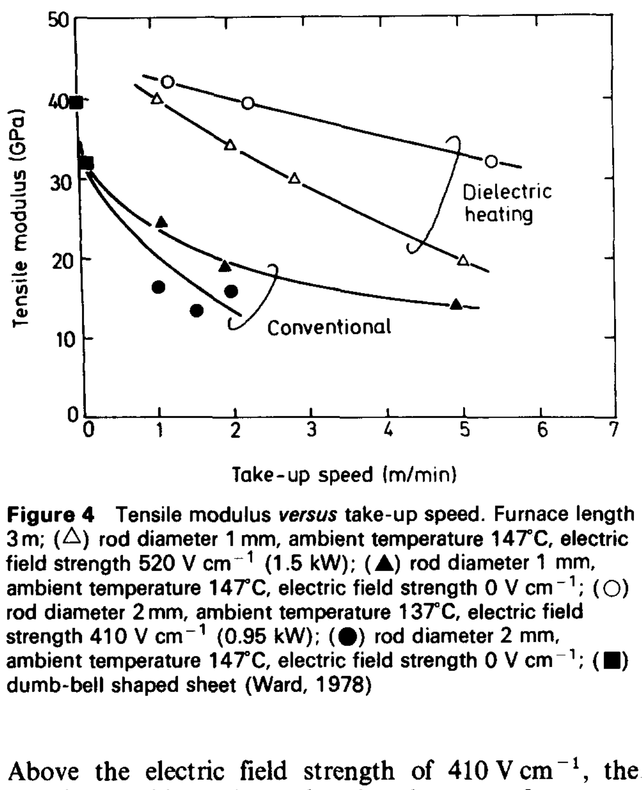

Figure 4 Tensile modulus *versus* take-up speed. Furnace length 3 m; (△) rod diameter 1 mm, ambient temperature 147°C, electric field strength 520 V cm^{-1} (1.5 kW); (▲) rod diameter 1 mm, ambient temperature 147°C, electric field strength 0 V cm^{-1}; (○) rod diameter 2 mm, ambient temperature 137°C, electric field strength 410 V cm^{-1} (0.95 kW); (●) rod diameter 2 mm, ambient temperature 147°C, electric field strength 0 V cm^{-1}; (■) dumb-bell shaped sheet (Ward, 1978)

Above the electric field strength of 410 V cm^{-1}, the drawing could not be undertaken because of runaway heating. In a dielectric heating, the sample is heated from the inside, so that rods with a larger diameter are more effectively heated than those with a smaller diameter under the same electric field strength. This is because the heat emission per unit volume from the surface is less in the wide rod than in the fine one. This is the reason why the rod with a diameter of 2 mm could not be drawn at the maximum electric field strength of 520 V cm^{-1} (maximum output of 1.5 kW). *Figure 3* shows that the highest tensile modulus of 39 GPa (draw ratio of 23) was obtained at an ambient temperature of 137°C under an electric field strength of 410 V cm^{-1} (0.95 kW). With no dielectric heating the highest tensile modulus was only 16 GPa (draw ratio of about 14).

Figure 4 shows the relationship between the tensile modulus and the take-up speed obtained from the drawing experiments for rods with diameters of 1 mm and 2 mm using the furnace with a length of 3 m. This Figure clearly shows the effect of drawing under dielectric heating. With conventional heating, in which the sample is heated from the outside, the drawing process becomes more difficult for wider rods at higher take-up speeds, because the inside of the rods cannot be heated sufficiently. On the other hand, with dielectric heating the sample is heated from the inside, so that the wide rods can be easily heated even at high take-up speeds. *Figure 4* shows that higher tensile moduli are obtained by the drawing with dielectric heating rather than with conventional drawing. The effect of drawing under dielectric heating is more remarkable for the wide rod (2 mmϕ) than for the fine rod (1 mmϕ). The higher tensile moduli are obtainable for the wide rod (2 mmϕ) than for the fine rod (1 mmϕ). This may be due to an insufficient electric field strength of 520 V cm^{-1} (maximum output of 1.5 kW) for the 1-mm rod.

Influence of ambient temperature, electric field strength, and strain rate

In the drawing under dielectric heating, the higher tensile moduli are obtainable for the wider rods. However, runaway heating is easily produced for the wider rods. Then, the influence of ambient temperature, electric field strength, and strain rate on the maximum draw ratio and the tensile modulus has been examined in detail for a POM tube with 3-mm o.d. and 1-mm i.d. Drawing conditions for the POM tubes are summarized in *Table 1*. The drawing experiments were operated at fixed feed speeds using the furnace with a length of 3 m. The tensile speed was gradually increased to raise the draw ratio. The feed speed was varied from 0.023 m min^{-1} to 0.50 m min^{-1}.

Figure 5 shows the ambient temperature dependence of tensile modulus at a constant electric field strength of 360 V cm^{-1} (0.70 kW). The highest tensile moduli are obtainable at an ambient temperature of about 140°C. This temperature is the crystalline absorption temperature of POM. This means that the temperature, at which molecular chains in the crystalline regions are rearrangeable, must be maintained by heating the sample from the outside, because the crystalline regions cannot be heated by the dielectric heating. Although the crystalline regions may be heated due to heat conduction, the effect is small, because the heat sources such as noncrystalline regions and defect regions within the lamellae are exhausted in the drawing process. *Figure 6* shows the electric field strength dependence of tensile modulus at a constant ambient temperature of 140°C. There is an optimum range of the electric field strength. Especially at a high electric field strength the drawing cannot be operated because of the runaway heating characteristic of dielectric heating.

As seen in *Figures 5* and *6*, the tensile modulus increases with decreasing feed speed. The strain rate γ is given by

$$\gamma = \frac{V - v}{L} = \frac{v}{L}(\lambda - 1)$$

where L is the furnace length, V and v are the take-up speed and the feed speed, respectively, and λ is the draw ratio. In these drawing experiments, the decrease of the feed speed corresponds to the decrease of the strain rate, because the furnace length is a constant value of 3 m. The

Table 1 Drawing conditions for POM tubes under dielectric heating. (Furnace length 3 m)

No.	Ambient temperature (°C)	Electric field strength (V cm^{-1})	Feed speed (m min^{-1})	Draw ratio	Strain rate (min^{-1})	Tensile modulus (GPa)
1	135	360	0.023	30	0.23	63
2	135	410		30	0.23	58
3	140	290	0.051	24	0.38	54
4	135	360		23	0.37	52
5	140	360		28	0.45	60
6	140	410		29	0.48	59
7	140	470		30	0.49	58
8	140	500		25	0.41	47
9	140	250	0.10	17	0.53	33
10	140	290		16	0.50	37
11	140	320		20	0.63	45
12	145	320		23	0.73	42
13	132	360		15	0.47	33
14	140	360		26	0.83	48
15	145	360		24	0.77	46
16	130	360	0.20	14	0.87	26
17	140	360		20	1.3	37
18	150	360		24	1.5	36
19	140	290	0.50	16	2.4	24
20	140	360		15	2.3	28
21	150	360		20	3.2	35
22	160	360		20	3.2	29
23	140	410		17	2.6	27

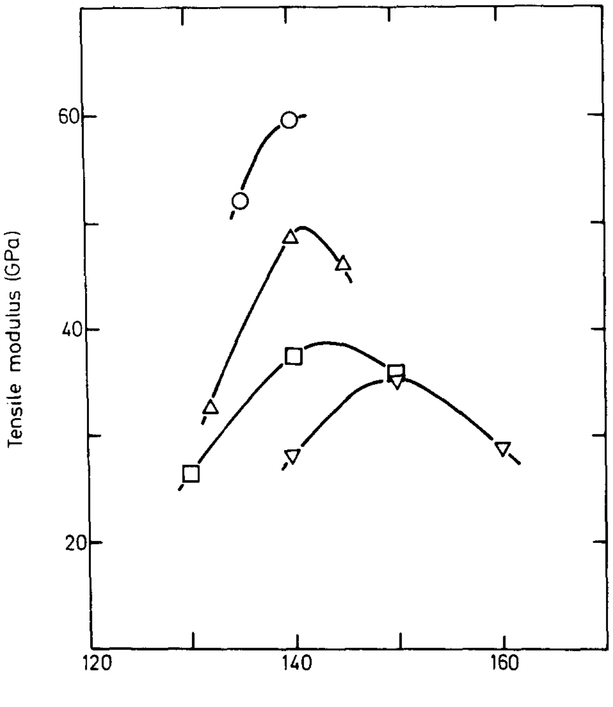

Figure 5 Tensile modulus *versus* ambient temperature at a constant electric field strength of 360 V cm^{-1} (0.70 kW) for POM tubes. Furnace length 3 m; feed speed (m min^{-1}): (○)0.051, (△) 0.10, (□) 0.20, (▽) 0.50

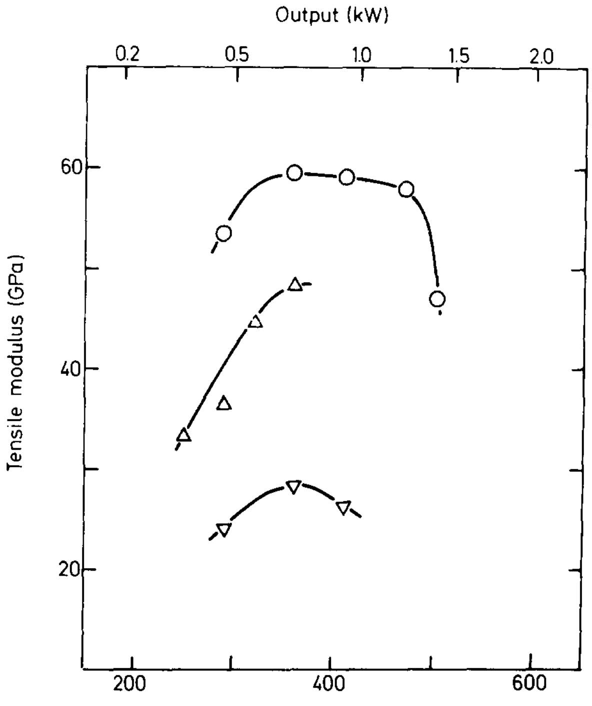

Figure 6 Tensile modulus *versus* electric field strength at a constant ambient temperature of 140°C for POM tubes. Furnace length 3 m; feed speed (m min^{-1}): (○) 0.051, (△) 0.10, (▽) 0.50

strain rates at each drawing condition are shown in *Table 1*. *Figure 7* shows the relationship between the tensile modulus and the strain rate. The tensile modulus increases with decreasing strain rate. For comparison, the literature values are also plotted in the same Figure. Clark and Scott[2] obtained a tensile modulus of 35 GPa for a POM fibre at a strain rate of 0.5 min^{-1}. Brew and Ward[3] obtained tensile moduli of 39.5 GPa and 32 GPa at tensile

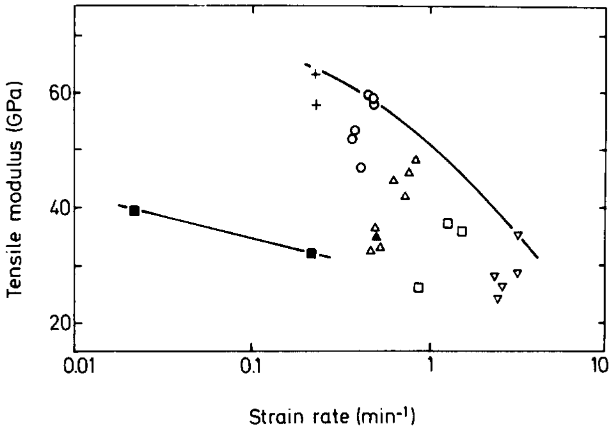

Figure 7 Tensile modulus *versus* strain rate for POM tubes. Feed speed (m min^{-1}): (+) 0.023, (○) 0.051, (△) 0.10, (□) 0.20, (▽) 0.50. (▲) Clark, 1974 (fibre), (■) Ward, 1978 (dumb-bell shaped sheet)

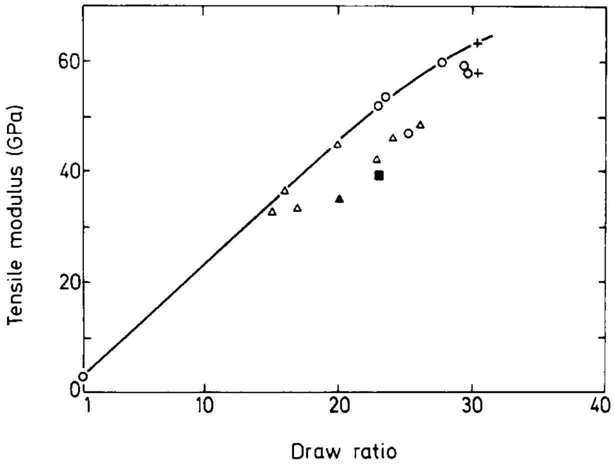

Figure 8 Tensile modulus *versus* draw ratio for POM tubes. Feed speed (m min^{-1}): (+) 0.023, (○) 0.051, (△) 0.10, (▲) Clark, 1974 (fibre), (■) Ward, 1978 (dumb-bell shaped sheet)

speeds of 1 cm min^{-1} and 10 cm min^{-1}, respectively, by drawing dumb-bell shaped POM samples. The strain rates are calculated to be 0.02 min^{-1} and 0.22 min^{-1}, respectively, from the tensile speeds, the draw ratio (23), and the sample size. Compared with the conventional data, higher tensile moduli are obtained at higher strain rates by the drawing under dielectric heating.

Figure 8 shows the relationship between the tensile modulus and the draw ratio for the POM tubes. The tensile modulus increases with an increase in draw ratio. In this new drawing process the samples were drawn up to the draw ratio of 30 and the highest tensile modulus of 63 GPa was obtained. Iguchi *et al.*[8] reported the value of approximately 100 GPa as the modulus of the POM whisker, i.e., almost equivalent to the ideal crystal modulus of POM. The highest tensile modulus obtained by this new drawing process attains about 60% of the ideal crystal modulus of POM. It is speculated that the achievement of such ultrahigh moduli is due to the fact that the stress by drawing is used effectively to orient the molecular chains in the noncrystalline regions and at defect regions within the crystal lamellae. This is because these regions are more highly heated than the crystalline regions during dielectric heating.

CONCLUSIONS

Ultrahigh modulus POM can be produced by drawing under dielectric heating at high ambient temperatures. The ambient temperature must be maintained near the crystalline absorption temperature at which the crystalline regions are rearrangeable, because the crystalline regions cannot be heated by the dielectric heating. Strain rate is one of the most important factors for obtaining ultrahigh modulus POM. High moduli are obtainable by drawing up to high draw ratios under low strain rates.

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