The effects of pressure on drawing polyoxymethylene: 1. Processing

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A new process has been developed for the continuous drawing of polymers under pressure. Draw ratios up to 34 were achieved by this process using polyoxymethylene. The pressure applied in the process acts effectively on the drawing behaviour, temperature, stress and velocity.

(Keywords: pressure effect; drawing process; drawing behaviour; polyoxymethylene; drawn fibre)

INTRODUCTION

Various techniques, such as tensile drawing under hydrostatic pressure in a closed pressure vessel, have been tried to produce high-modulus polymers. The influence of pressure on deformation and mechanical properties of polymers have also been investigated[1–6]. However, since these experiments were performed at room temperature, the polymers were less ductile and almost brittle near the yield point. The methods so far used are impracticable owing to discontinuity. Thus, a new process for the continuous drawing of polymers under high pressure was developed[7]. The present work comprises three parts. The first presents the characteristics of the process and pressure effects on drawing of polymer tubes using polyoxymethylene (POM). The second part discusses the effects of pressure on the structure and properties of drawn POM fibres. The third part deals with the effects of voids on the chemical resistance of drawn POM fibres.

EXPERIMENTAL

Drawing process

The process consists of continuous two-step drawing. *Figure 1* shows the outline of the apparatus, which mainly comprises a creel, feed belt, take-up belt, winder, pressure vessel, pump, heater, pressure control valve and tensiometer. Polymer material (A) is supplied to the pressure vessel (3) through the feed belt (2) from the creel (1), taken up by the take-up belt (5), continuously supplied to the second pressure vessel (6), taken up by the take-up belt (8) and wound by the winder (9). The cylindrical pressure vessels, which have holes at both ends through which material of continuous length passes, are filled with pressurized fluid. Silicone oil was generally used as the pressurized fluid. The holes have seals that allow the polymer to pass smoothly and maintain the pressure in the vessels. The polymer is pressurized by the fluid while passing into the pressure vessels, heated by preheated fluid, pulled by the take-up belts (5, 8) and wound by the winder. The pressurized fluid is heated by the heaters (14, 15) situated in the fluid circulating tanks. The heated fluid is circulated between the fluid circulating tanks and pressure vessels by pumps (10,11). The outside of the pressure vessels is covered with an insulator (16, 17) to maintain the temperature of the fluid. The pressure is regulated by the pressure control valves (12, 13). The drawing tension at the first and second steps is measured by the loadcell-type tensiometers (4, 7) situated between the pressure vessels and take-up belts. The polymer is continuously drawn to produce fibres of continuous length.

Sample preparation

A tube with an outer diameter of 6.0 mm and inner diameter of 1.8 mm was prepared by melt extrusion of an acetal homopolymer 'Tenac 3010' (Asahi Chemical Industry Co. Ltd; number-average molecular weight M_n, 63 000; apparent density, 1.42 g cm^{-3}; softening point, 174°C; melting point, 179°C). The tube was continuously drawn by pressurized drawing to obtain rod-like drawn fibres (pressurized drawn fibres), under the following conditions:

(i) First step—first pressure vessel length, 2 m; feed speed, 0.4 m min^{-1}; take-up speed, 3.2 m min^{-1}; draw ratio, 8; drawing temperature, 155°C; pressure, 50 kg cm^{-2}.

(ii) Second step—second pressure vessel length, 12 m;

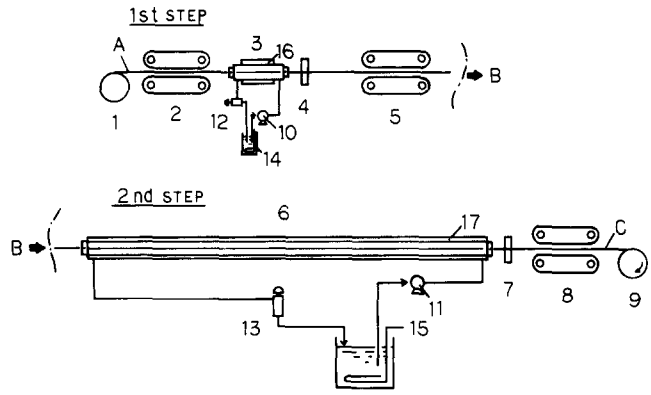

Figure 1 The apparatus for the pressurized drawing process: (A) POM material, (B, C) drawn POM fibre, (1) creel, (2) feed belt, (5, 8) take-up belts, (3, 6) pressure vessels, (4, 7) tensiometers, (10, 11) pumps, (12, 13) pressure control valves, (14, 15) heaters, and (16, 17) insulation

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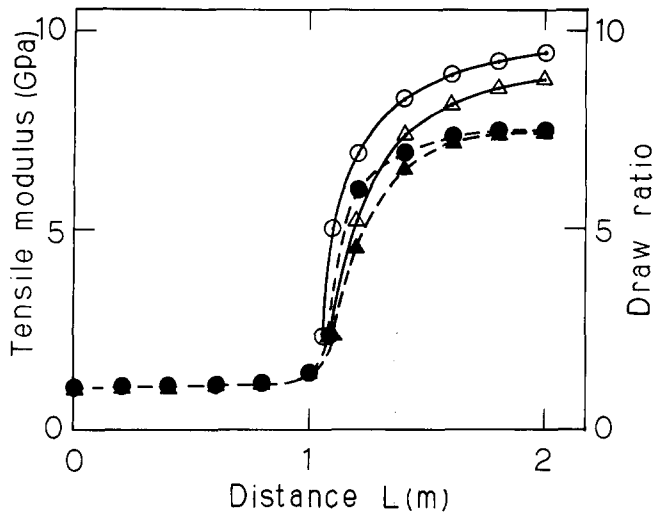

Figure 2 Tensile modulus and draw ratio vs. distance L from the entrance of the pressure vessel in the first step: (○, ●) pressurized drawn fibre; (△, ▲) conventional drawn fibre. The full and broken curves indicate the tensile modulus and draw ratio, respectively

feed speed, 3.2 m min^{-1}; take-up speed, 8.0 m min^{-1}; draw ratio, 2.5 (total 20); drawing temperature, 174°C; pressure, 400 kg cm^{-2}.

Silicone oil (Toray Co. Ltd, silicone oil WF30) was used as the pressurizing and heating medium. For comparison, conventional drawing in silicone oil and heated dry air was carried out using the same apparatus and conditions as for the pressurized drawing except for a gauge pressure of 0 kg cm^{-2}. Hollow drawn fibres were obtained. The fibres were washed several times in fresh Freon-113 by extraction and dried at room temperature.

Measurements

Actual drawing stress was determined from drawing tension and cross-sectional areas of drawn fibres while passing through the loadcell-type tensiometer. The draw ratio was calculated from the ratio of sample weight per unit length before and after drawing. Tensile modulus along the fibre axis was measured at room temperature using an Instron tensile testing machine according to JIS K7113 (1981). The modulus was determined from slopes of stress–strain curves using an extensiometer. The cross-sectional area of the sample for calculating the modulus was determined from the sample diameter. The outer diameter was measured with a micrometer and the inner diameter was found from a photograph of the cross-section. D.s.c. measurement was carried out at a heating rate of 8°C min^{-1} and a sample weight of 3.0 mg.

RESULTS AND DISCUSSION

A POM tube was drawn up to a draw ratio of 32 and the fibre thus obtained had a maximum tensile modulus of 56 GPa. The processing is usually conducted between 4 and 40 MPa, and is comparatively easy.

Properties of drawn fibres

The draw ratio and tensile modulus of a drawn fibre at each position of the first and second pressure vessels were examined. The fibre inside the drawing vessels was taken out as follows. Operation of the apparatus was brought to a stop immediately after the drawing. The temperature was cooled to room temperature while keeping the fibre end fixed at each belt, and the fibre was then taken out.

First-step drawing

Figure 2 shows changes in the tensile modulus and draw ratio along the fibre length, as measured from the entrance of the pressure vessel in the first-step drawing. Both pressurized and conventional drawing in silicone oil showed necking. Necking in both cases began at $\lambda = 5.5$ and was generated at lengths of 1.2 and 1.4 m from the entrance of the vessel, respectively. In the latter under the condition of dry heated air, the undrawn part and necked part protruded from the exit of the device by as much as ~20 cm. The fibre fractured at the neck, possibly due to poor heat capacity and conductivity of air compared with silicone oil. The melting behaviour of the drawn fibre ($\lambda = 8$) was examined using d.s.c., and the results are shown in *Figure 3*. Both samples showed essentially the same unsymmetrical d.s.c. curve with an endothermic peak at 182.4°C, thus being 4.4°C higher than the temperature of the undrawn POM tube.

The second-step drawing

Figure 4 shows modulus change during the second-step drawing. The draw ratio and tensile modulus increased considerably in the first half and gradually so in the latter half of the vessel in the pressurized drawing. The same

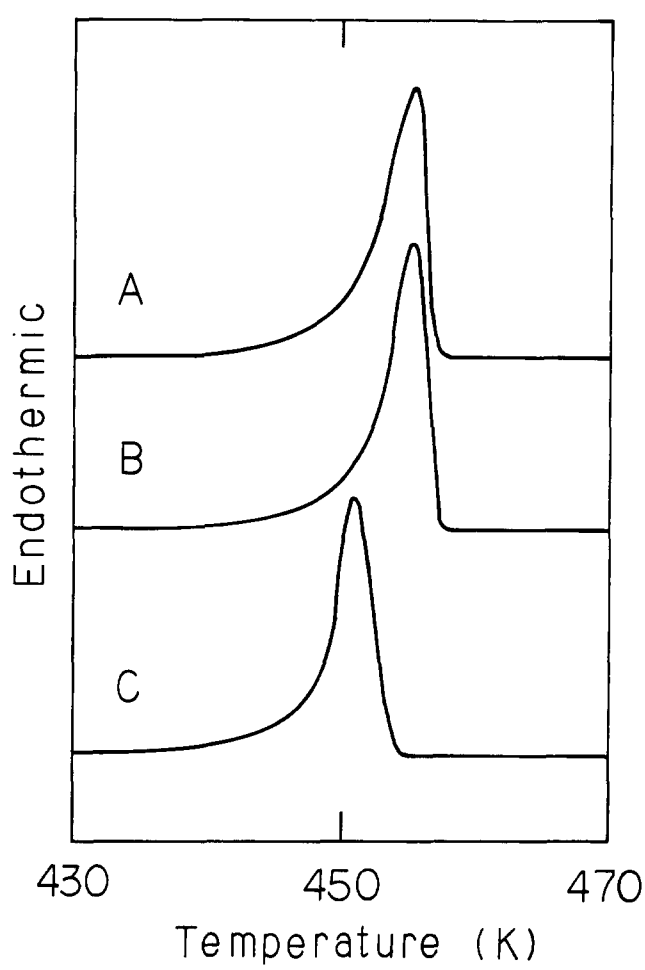

Figure 3 D.s.c. melting thermograms of the drawn fibres ($\lambda = 8$): (A) pressurized drawn fibre; (B) conventional drawn fibre; (C) undrawn POM tube

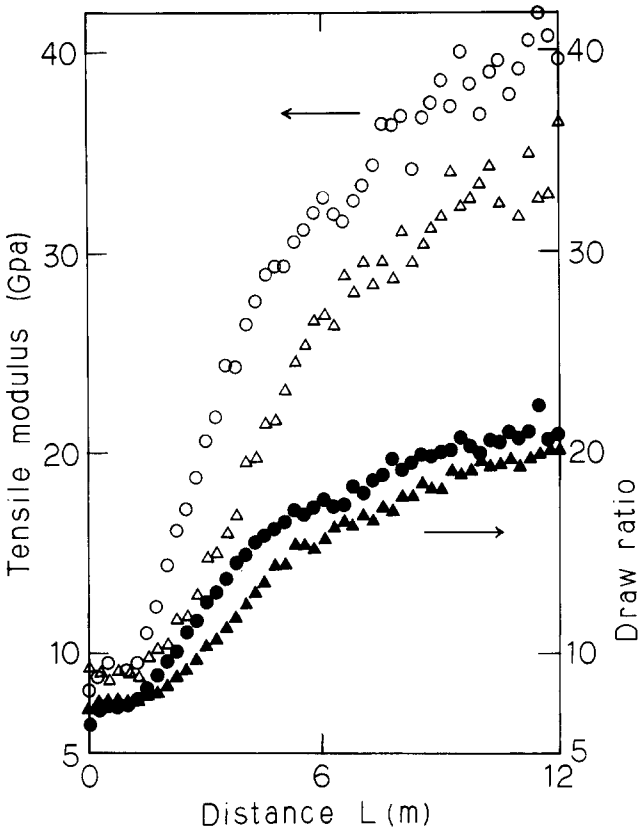

Figure 4 Tensile modulus and draw ratio vs. distance L from the entrance of the pressure vessel in the second step: (○, ●) pressurized drawn fibre; (△, ▲) conventional drawn fibre. The full and open symbols indicate the draw ratio and tensile modulus, respectively

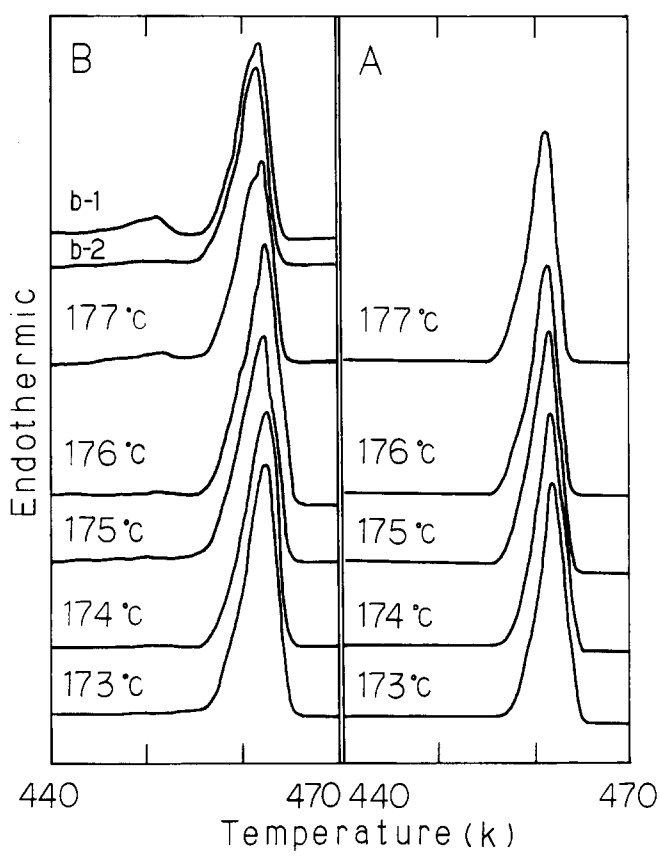

Figure 5 D.s.c. melting thermograms of the drawn fibres ($\lambda = 20$) prepared at constant temperatures of 173–177°C: (A) pressurized drawn fibres; (B) conventional drawn fibres; (b-1) inside, drawn at 177°C; (b-2) outside, drawn at 177°C

was noted for the conventional drawing, except for the relatively small modulus.

Drawn fibres of $\lambda = 20$ were prepared under the same conditions as above except at temperatures of 173–177°C in the second step, and were examined for tensile modulus and melting behaviour. Melting behaviour was examined in bulk, outside and inside the sample (outer diameter ~1.3 mm). A portion of the sample cut to 0.4 mm thickness from the surface was the outside, and the remainder was the inside.

Figure 5 shows the d.s.c. curves of these samples. The pressurized drawn fibres prepared at constant temperatures of 173–177°C showed an endothermic peak at 189°C in bulk, both outside and inside. The conventional samples prepared in silicone oil at 173–177°C showed an endothermic peak at 188°C in bulk, both outside and inside. However, the bulk at 177°C showed a small endothermic peak at 178°C in addition to the main peak at 188°C. The small peak at 178°C could be easily observed in the inside but not the outside. The peak temperature at 178°C was equal to that of the undrawn tube, as in *Figure 3*.

Thus, the tesile modulus and ratio of the heats of fusion at 178°C to the total heat of fusion on the d.s.c. curve, $\Delta H(177)/\Delta H(\text{all})$, were measured for each sample. The results are shown in *Figure 6*. The pressurized sample showed no change in the modulus with draw temperature and was zero for $\Delta H(177)/\Delta H(\text{all})$ in the range of

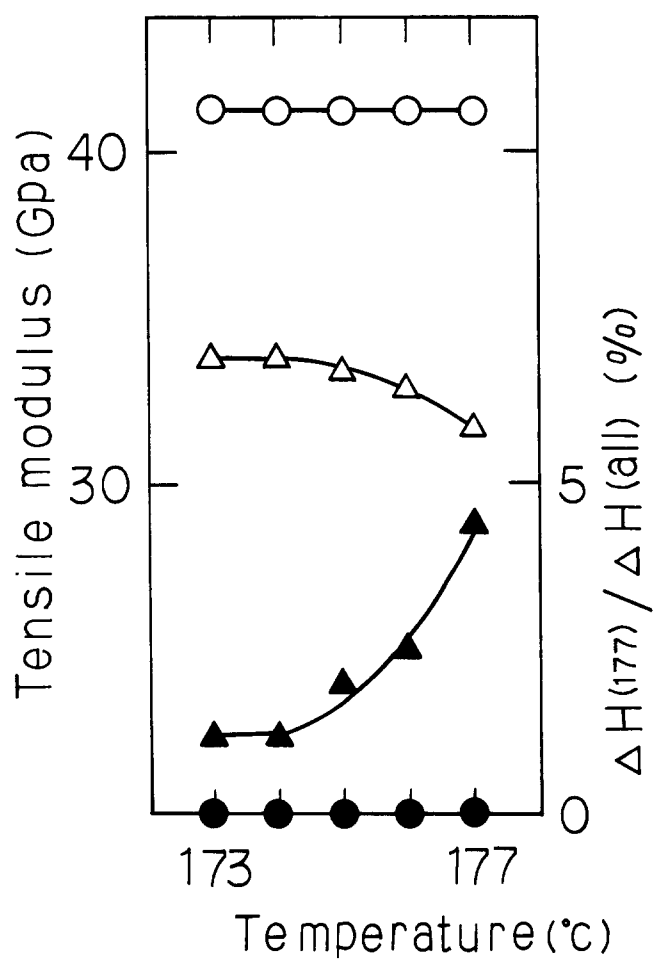

Figure 6 Tensile modulus and the ratio $\Delta H(177)/\Delta H(\text{all})$ vs. drawing temperature in the second step: (○) tensile modulus for pressurized fibres; (△) tensile modulus for conventional fibres; (●) $\Delta H(177)/\Delta H(\text{all})$ of pressurized fibres; (▲) $\Delta H(177)/\Delta H(\text{all})$ of conventional fibres

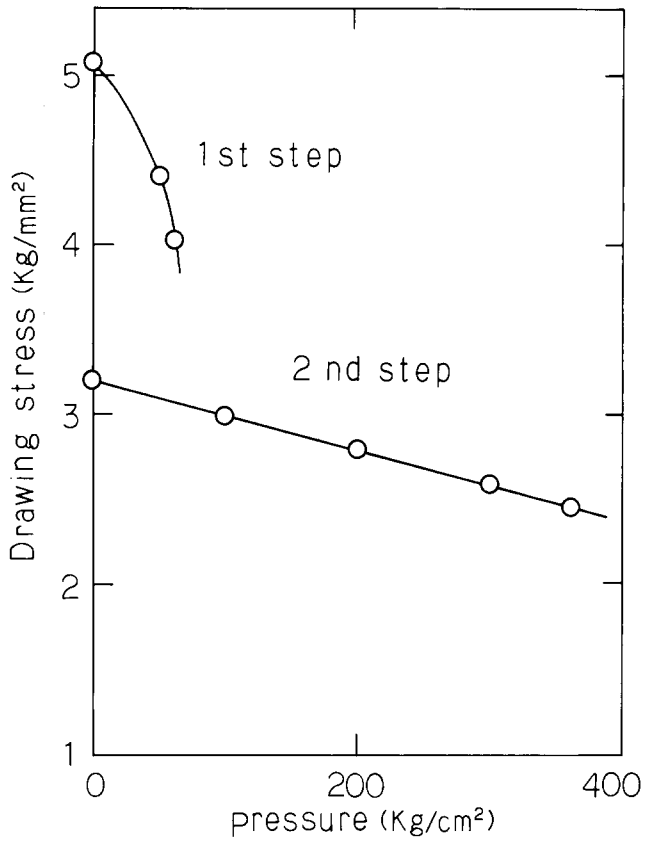

Figure 7 Drawing stress vs. pressure: first-step drawing ($\lambda=8$) at 165°C and second-step drawing ($\lambda=20$) at 174°C

173–177°C. The conventionally drawn samples, however, exhibited a decrease in the modulus and a rapid increase in $\Delta H(177)/\Delta H(\text{all})$ above 176°C. The following reasons may explain this: (1) a portion at 178°C, situated at the foot of the d.s.c. curve (*Figure 3*) of the first-step drawn sample ($\lambda=8$), remained to some extent without completely shifting to the peak of 188°C after the second-step drawing; (2) the inside of the drawn fibre was overheated during the second-step drawing.

The above situation was noted for drawing at 177°C, close to the melting point of the undrawn POM, and thus the latter reason appears applicable. Essentially the same has been observed in the case of the ultra-drawn fibre prepared from a large-diameter POM precursor tube by microwave heating/drawing as reported by Nakagawa *et al.*, and explained in terms of partial melting due to microwave overheating in the inside[8]. Although the origin of the lower peak could not be determined, it was observed even in conventional drawing, with heat being supplied from the surface of the fibre. This indicates the possibility of an overheating mechanism. Indeed, a significant amount of heat is evolved during tensile deformation of a polymer. The pressurized drawn fibre was homogeneous even at 177°C, possibly owing to increased supercooling under applied pressure. The melting point of POM rises with increase in pressure (2°C per 100 kg cm^{-2})[9]. This effect thus appears to be efficiently exerted in the process.

Effects of pressure on drawing stress

Figure 7 shows drawing stress vs. pressure for the first ($\lambda=8$) and second-step drawing ($\lambda=20$), the former exceeding the latter. One-step superdrawing thus apparently leads to fracture before high draw ratios since unnecessary high drawing stress is brought to bear on the fibre after necking. In fact, it was at most $\lambda=16$ through one-step drawing even at a low speed. Drawing stress decreased as pressure increased. The tendency changed with drawing temperature. As shown in *Figure 8*, the effect of pressure was clearly observed above 145°C and quite evident with increase in temperature. It thus follows that the pressure applied in the transverse direction of the material is transmitted in the drawing direction and acts to promote drawing.

Pressure effect on the strain rate

The relationship between strain rate (γ) and tensile modulus in the first-step and second-step drawing was determined by:

$$\gamma=(V-v)/L \qquad (1)$$

where V, v and L are the take-up speed, feed speed and length of the pressure vessel in each step. Drawing was carried out as follows. An undrawn POM tube with outer diameter of 6.0 mm and inner diameter of 1.8 mm was drawn at $\lambda=8$ in the first step, and the take-up speed was increased up to the point of ductile fracture in the second step. In the first step, the drawing temperature was 155°C, pressure 40 kg cm^{-2} and feed speed varied from 0.02 to 9 m min^{-1}. In the second step, the temperature was 160°C at $\gamma\leqslant 0.2\,\text{min}^{-1}$, 174°C at $\gamma>0.2\,\text{min}^{-1}$, and pressure 400 kg cm^{-2}. Conventional drawing was carried out under the same conditions as pressurized drawing except for a gauge pressure of 0 kg cm^{-2}.

Thus, the strain rate of the first step (γ_1) was

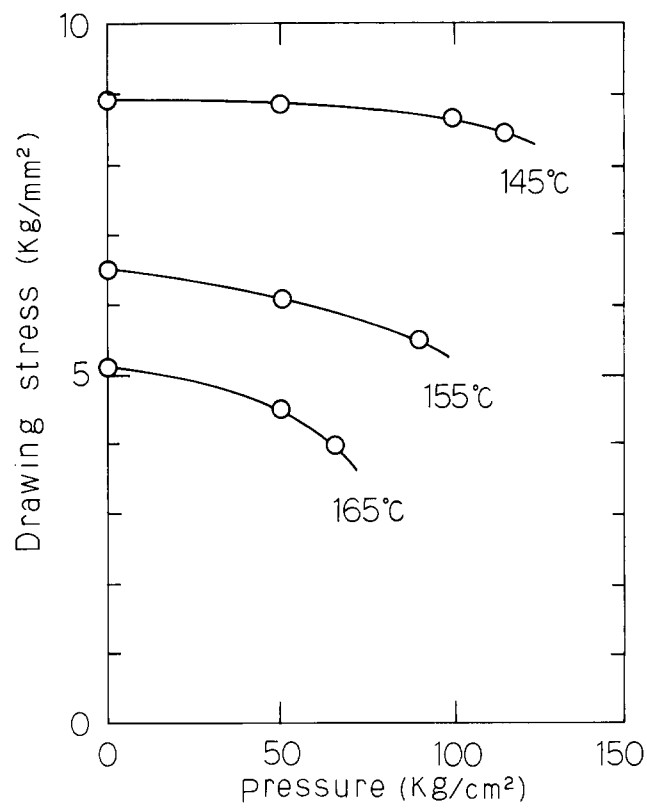

Figure 8 Drawing stress vs. pressure at several temperatures in the first-step drawing

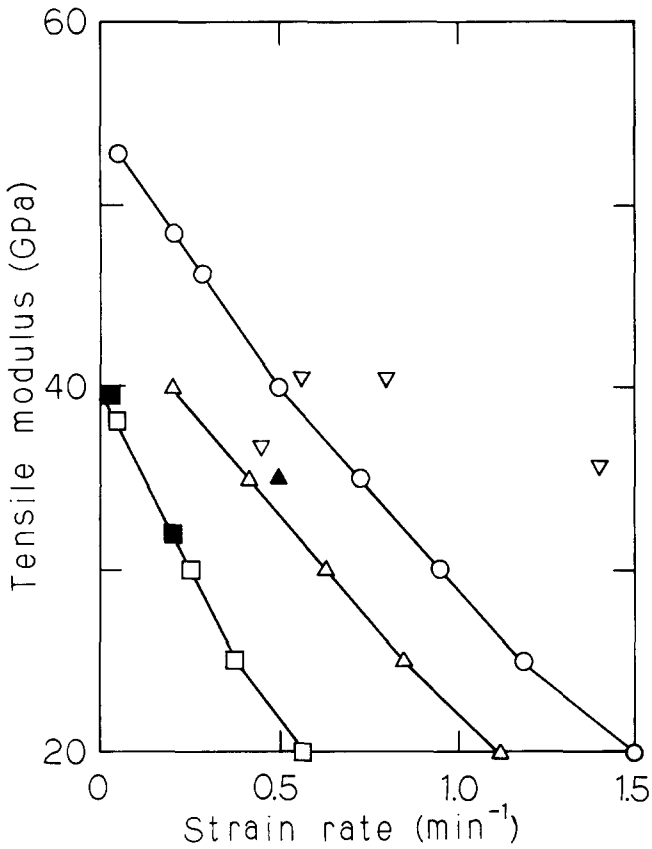

Figure 9 The maximum tensile modulus achieved vs. strain rate: (○) pressurized drawing; (△) conventional drawing in silicone oil; (□) conventional drawing in air; (▲) Clark and Scott[10], (■) Brew and Ward[11], (▽) Nakagawa *et al.*[12]

$\sim 15\,min^{-1}$ for both cases in silicone oil, and $12\,min^{-1}$ for the conventional one in air. *Figure 9* shows the strain rate (γ_2) vs. maximum tensile modulus (E_{max}) in the second step. The values obtained by Clark and Scott[10], Brew and Ward[11] and Nakagawa *et al.*[12] are also plotted. The E_{max} decreased with increase in γ_2. The values of γ_2 for $E_{max} = 53$ GPa ($\lambda = 34$, void ratio $\sim 10\%$), 40 GPa ($\lambda = 19.5$) and 20 GPa ($\lambda = 10$) were 0.05, 0.5 and $1.5\,min^{-1}$, respectively, in the pressurized drawing. For conventional drawing in silicone oil and in heated air γ_2 values were 0.2 and $0.02\,min^{-1}$, respectively, for $E_{max} = 40$ GPa, and 1.1 and $\sim 0.5\,min^{-1}$, respectively, for $E_{max} = 20$ GPa. For $E_{max} = 20$ GPa γ_2 was at most one-tenth larger than γ_1. This means that the rate-determining stage of the drawing is in the second step and γ through the full step is determined by γ_2. The overall γ of the pressurized drawing is thus about 2.5 times that of the conventional one in silicone oil and 25 times the conventional one in air for $E_{max} = 40$ GPa.

Some reports indicate the strain rate of superdrawing POM. Clark *et al.*[10] obtained a tensile modulus of 35 GPa for a drawn fibre ($\lambda = 20$) at a strain rate of $0.5\,min^{-1}$, and Brew *et al.*[11] a tensile modulus of 39.5 GPa and 32 GPa by drawing a dumbbell-shaped sample at strain rates of 0.02 and $0.2\,min^{-1}$, respectively. Nakagawa *et al.*[12] obtained dynamic moduli corrected for void ratios of 54 GPa ($\lambda = 28$), 54 GPa ($\lambda = 28$), 54 GPa ($\lambda = 33$) and 51 GPa ($\lambda = 34$) by drawing a POM tube with outer diameter of 4 mm and inner diameter of 1 mm at strain rates of 0.45, 0.56, 0.8 and $1.4\,min^{-1}$, respectively. The dynamic moduli of 54, 54, 54 and 51 GPa were determined as apparent moduli of 36.7, 40.5, 40.5 and 35.7 GPa, respectively, from the void ratio in the literature[12]. The strain rates of conventional drawing in air in this work are comparable to those used by Brew and Ward[11]. The draw rate for the conventional drawing in silicone oil was shown to be 10 times that in air. The strain rate of pressurized drawing is at the same high level as that of microwave drawing, although the strain rate depends on several factors such as precursor size, geometry and molecular weight.

CONCLUSIONS

We have developed a new process for drawing polymers under pressure and applied it to POM. Superdrawing to a draw ratio of 34 was achieved, and many characteristics of the process were elucidated. By this process, efficient drawing under comparatively low pressure is easily possible. On using a liquid as both the pressure and the heating media, rapid and uniform heating of the material is possible. Thus, polymers with large diameter can be uniformly drawn. The process involves less drawing stress. These characteristics are favourable for the high-speed superdrawing of polymers.

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