Microwave heat-drawing of polyoxymethylene: Influence of tensile load and precursor size

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The influence of tensile load and precursor size on the drawing behaviour of polyoxymethylene tubes, with outer diameters of 3, 4 and 6 mm, has been studied at a feed speed of 6 cm min^{-1} under microwave heating. As the temperatures of sample portions are difficult to measure, tensile load is used as a corresponding parameter. It is shown that there is an optimum tensile load for a given tube diameter to achieve high modulus and high strength over all draw ratios. The optimum tensile load gives rise to uniform heating which is confirmed by differential scanning calorimetry. The attainable dynamic modulus decreased from 59 GPa to 51 GPa with increase in the precursor tube diameter from 3 to 6 mm.

(Keywords: polyoxymethylene; microwave heating; drawing; tensile load; dynamic modulus)

INTRODUCTION

It has been shown that ultra-high-modulus polyoxymethylene (POM), having tensile moduli of about 60 GPa (draw ratio greater than 30), can be produced by a microwave heat-drawing technique[1–4]. In conventional drawing techniques, the draw temperature can be specified[5–8]. However, it is difficult to measure sample temperatures during the microwave heating process. Tensile load is used as a parameter instead of the draw temperature in the microwave heat-drawing technique[4]. The influence of tensile load on the drawing behaviour of POM tubes has been studied under microwave heating. The resultant mechanical properties and melting behaviour have been examined. One of the features of microwave heating is inner heating, which enables the heating of wide samples. So, the influence of tube size on drawing behaviour has also been investigated.

EXPERIMENTAL

Materials

The polymer used was a commercial grade of POM: Tenac 3010 (Asahi Chemical Industry Co., Japan). The number-average molecular weight was stated to be 63 000, the density 1.42 g cm^{-3} and the melting point 175°C. Tubes with outer diameters of 3, 4 and 6 mm were prepared from pellets by extrusion. The inner diameters of all the tubes were 1 mm. These tubes were used for the drawing experiments.

Drawing

The microwave heating furnace was divided into two furnaces. The front furnace (0.5 m long) was used to make a neck point, while the rear furnace (3 m long) was used for ultra-drawing the sample. Electric heaters were mounted around the furnaces in order to control the ambient temperature on the insides of the furnaces. For the rear furnace, the electric heaters were divided into six sections (No. 2 through No. 7) along the draw direction, as shown in *Figure 1*, and each temperature was controlled independently. The tensile load during the process was monitored with a tension meter. All drawing experiments were made at a feed speed of 6 cm min^{-1}. Details of the apparatus and the drawing procedure have been given previously[4].

Measurements

The dynamic mechanical measurements were performed at room temperature and at a frequency of 3.5 Hz on samples 70 mm long using a Rheovibron DDV-3-EA (Toyo Baldwin Co., Japan). The tensile strength and the elongation at break were measured on a tensile testing machine, Strograph T (Toyoseiki Works, Japan). The sample length was 100 mm and the crosshead speed was 100 mm min^{-1}. The cross-sectional areas were determined by weighing the samples, and using a density value of 1.42 g cm^{-3}. The melting behaviour of drawn samples was examined using a Perkin–Elmer DSC-2. The measurements were made at a heating rate of 10°C min^{-1} on samples weighing 5 mg.

RESULTS AND DISCUSSION

Influence of tensile load

The influence of tensile load on the drawing behaviour was examined using tubes with outer diameter of 4 mm. It has already been shown in a study on the grade dependence of the optimum drawing conditions for high modulus and high strength that the optimum tensile load and the ambient temperature are 19 kg and 120°C, respectively, for these tubes[4]. So, the ambient temperatures of heaters No. 4 through No. 7 in the rear furnace were fixed at 120°C, while the ambient temperatures of No. 2 and No. 3 were adjusted to give a

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maximum dynamic modulus at a given tensile load. The ambient temperature (No. 1) of the front furnace was kept at 30°C. The tensile load was changed in the range of 12 kg to 21.5 kg. The take-up speed was automatically controlled to hold a given tensile load. The microwave power of the front furnace was emitted to make a neck point, and then the output of the rear furnace was gradually increased. With increase in the output, the take-up speed increased to maintain the tensile load, i.e. the draw ratio increased.

Drawing conditions for maximum dynamic moduli at different tensile loads are summarized in *Table 1*. The tensile load reflects the sample temperature. At a given draw ratio, the tensile load increases as the sample temperature decreases. Also, the tensile load increases with increase in the draw ratio at a given sample temperature. Therefore, using the above drawing conditions, the sample temperature should decrease with increase in the tensile load. In fact, the outputs were depressed with increase in the tensile load.

It has been shown that the sample diameter gradually decreases over the rear furnace length under optimum drawing conditions[4]. The changes of outer diameters in the furnaces under optimum drawing conditions at different tensile loads are shown in *Figure 1*. Almost all the samples decrease gradually in diameter in the rear furnace. However, at a tensile load of 17 kg, the diameter change is a little different from the others, i.e. the diameter appears to have decreased rapidly at section No. 5. It seems that the drawing conditions were not necessarily optimum at the tensile load of 17 kg.

The tensile load dependences of maximum draw ratio and dynamic modulus are shown in *Figure 2*. The draw ratio was calculated from the precursor and product cross-sectional areas. The maximum draw ratio increased with decrease in the tensile load, i.e. with increase in the sample temperature. The dynamic modulus reached a maximum at a tensile load of 19 kg. At this optimum tensile load, the take-up speed was stable, i.e. an almost constant draw ratio was obtained, and the scattering of the dynamic modulus value was small.

The draw ratio dependences of dynamic moduli for tubes drawn at different tensile loads are shown in *Figure 3*. The drawing conditions at a given draw ratio were the same as the conditions in *Table 1*, except for the output of the rear furnace. The output was increased to increase the draw ratio. Therefore, the sample temperature rose with increase in the draw ratio at a given tensile load. The highest dynamic moduli were obtained at the optimum tensile load of 19 kg over all the draw ratios.

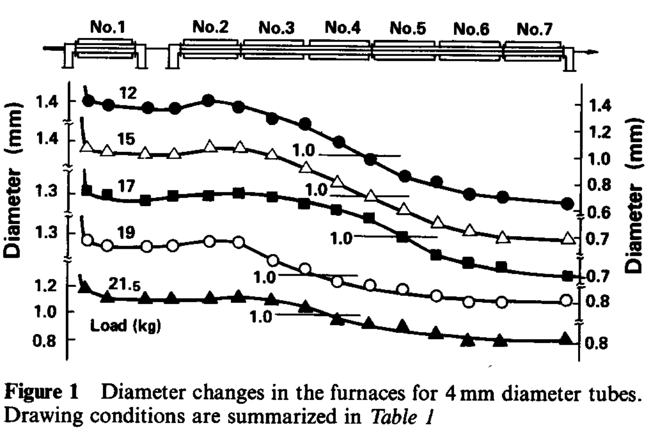

Figure 1 Diameter changes in the furnaces for 4 mm diameter tubes. Drawing conditions are summarized in *Table 1*

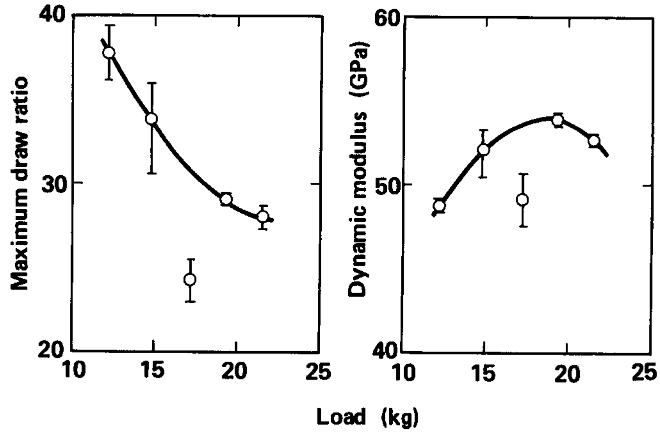

Figure 2 Maximum draw ratio and dynamic modulus *versus* tensile load for 4 mm diameter tubes

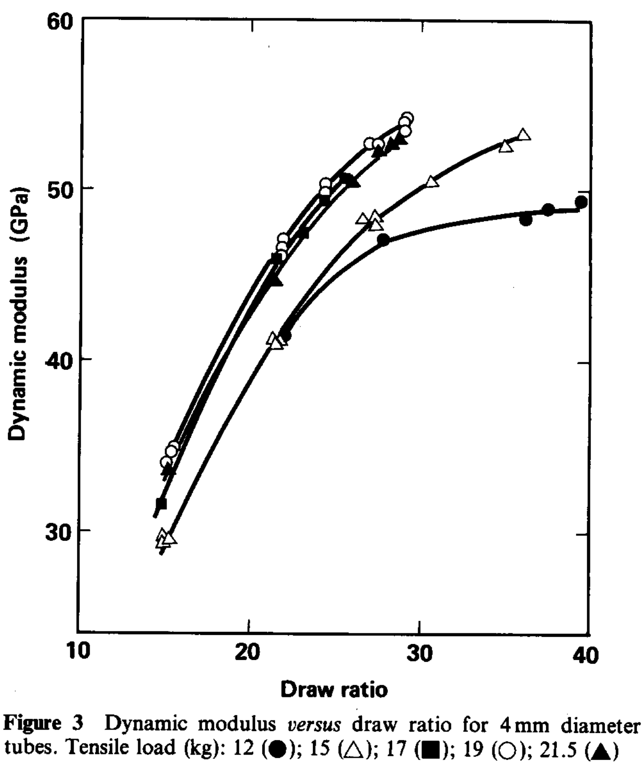

Figure 3 Dynamic modulus *versus* draw ratio for 4 mm diameter tubes. Tensile load (kg): 12 (●); 15 (△); 17 (■); 19 (○); 21.5 (▲)

Table 1 Drawing conditions for tubes of 4 mm diameter

Symbol	Load (kg)	Output (kW)		Ambient temperature (°C)							Maximum draw ratio	Dynamic modulus (GPa)
		Front	Rear	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7		
●	12	1.0	0.5	30	80	110	120	120	120	120	38	49
△	15	1.0	0.4	30	80	110	120	120	120	120	34	52
■	17	0.9	0.4	30	90	110	120	120	120	120	24	49
○	19	0.8	0.4	30	110	120	120	120	120	120	29	54
▲	21.5	0.7	0.3	30	120	120	120	120	120	120	28	53

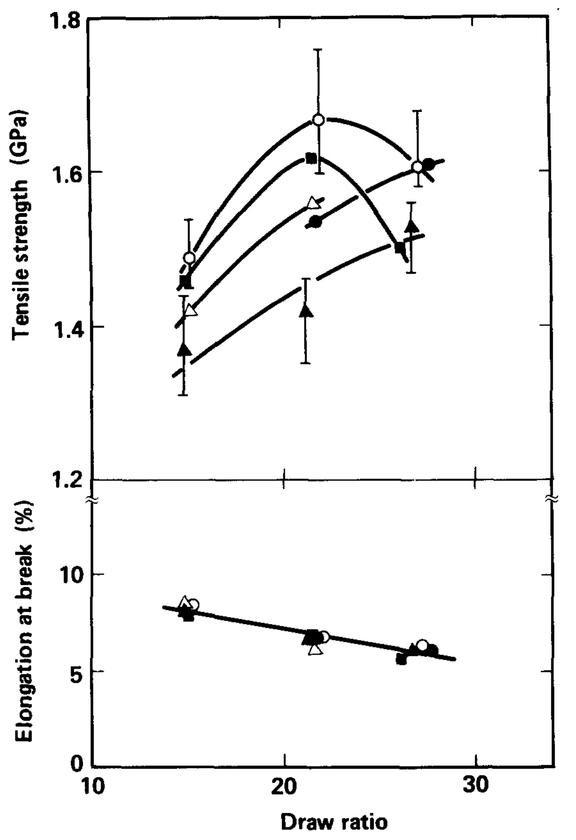

Figure 4 Tensile strength and elongation at break *versus* draw ratio for 4 mm diameter tubes. Tensile load (kg): 12 (●); 15 (△); 17 (■); 19 (○); 21.5 (▲)

The draw ratio dependences of tensile strength and elongation at break are shown in *Figure 4*. The highest tensile strengths were also obtained at the optimum tensile load of 19 kg. The tensile strengths of tubes drawn at a tensile load of 21.5 kg were lowest. No dependence of the elongation at break on the tensile load was observed.

As mentioned above, highest modulus/highest strength tubes were prepared at a tensile load of 19 kg over all the draw ratios. To understand why the highest values were obtained at this tensile load, the melting behaviour of tubes with different draw ratios prepared at different tensile loads was examined. The d.s.c. melting endotherms of drawn samples are shown in *Figure 5*. Single melting peaks were observed at the optimum tensile load of 19 kg and also at a tensile load of 17 kg over all the draw ratios. However, an additional, small melting peak was observed slightly below the main peak for other tensile loads.

At lower tensile loads, the subpeaks, which are lower by about 10°C than the main peaks, increase with decrease in the tensile load and with increase in the draw ratio. The decrease of the tensile load and the increase of the draw ratio correspond to the increase of the sample temperature, which was raised with microwave heating. The drawn samples with subpeaks were divided into outer and inner sections. The d.s.c. measurements were made separately for these sections. As an example, melting endotherms of both sections of the sample drawn up to a draw ratio of 28 under a tensile load of 12 kg are shown in *Figure 6a*. A subpeak was observed only for the inner section of the sample. From the fact that the

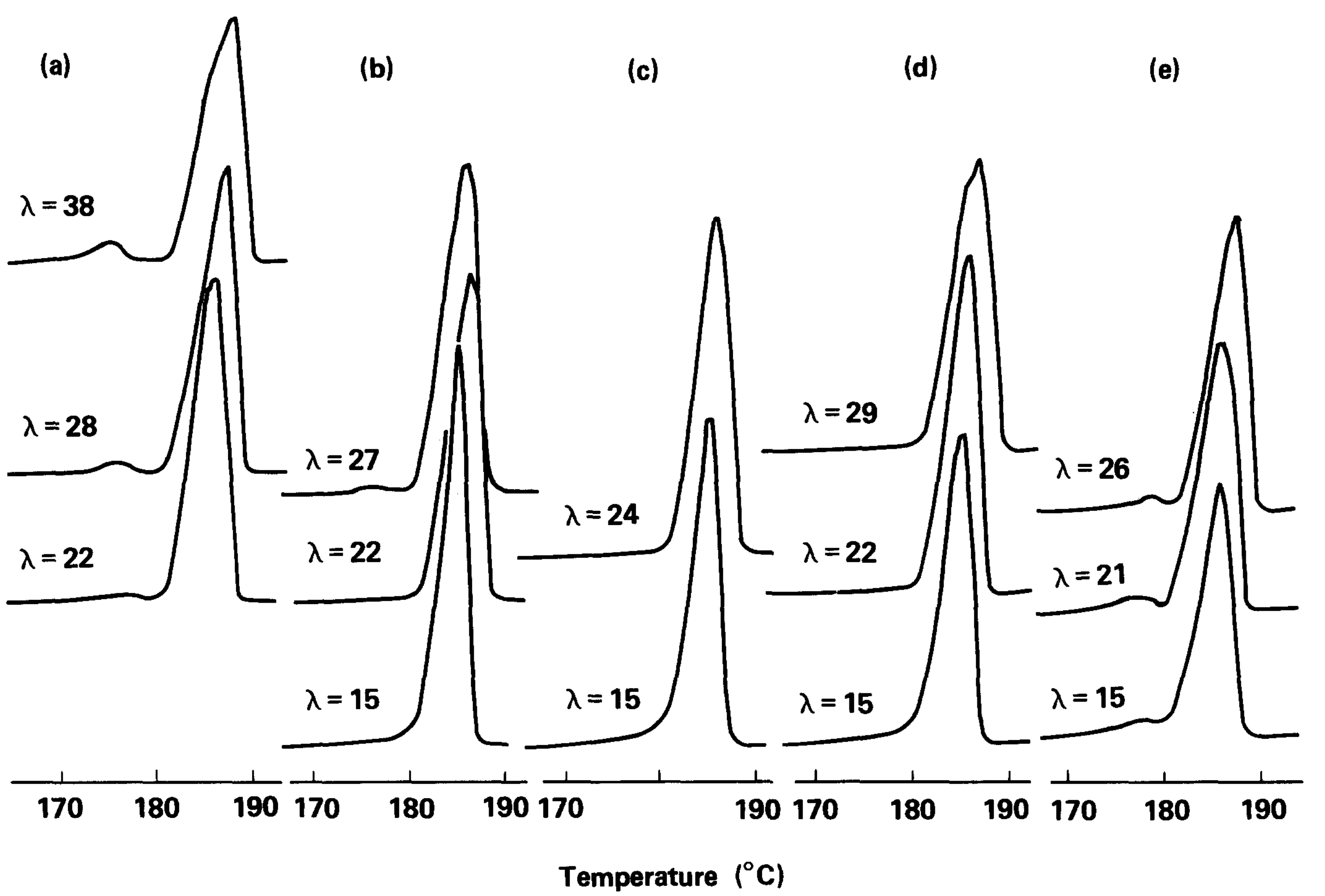

Figure 5 D.s.c. melting endotherms of drawn samples. Precursor tube: 4 mm diameter. Tensile load (kg): (a) 12; (b) 15; (c) 17; (d) 19; (e) 21.5

microwave heating is inner heating, it seems that the occurrence of the subpeak at the lower tensile loads is due to excess microwave heating of the inner sections.

The subpeaks were observed even at the highest tensile load of 21.5 kg. However, the increase of the subpeak with increase in the draw ratio was not clear and the subpeaks were observed in both sections, as shown in *Figure 6b*. Therefore, the occurrence of the subpeak in this case is not due to excess microwave heating. In fact, the outputs of the microwave were lowest, as shown in *Table 1*. A high tensile load corresponds to a low sample temperature. At the tensile load of 21.5 kg, the sample temperature may be too low to rearrange the molecular chains sufficiently into extended chains in the crystallites. The subpeaks may be due to the melting of small crystallites, which partially remained in the POM. The optimum tensile load of 19 kg gives rise to uniform heating sufficient to rearrange the molecular chains in the crystallites.

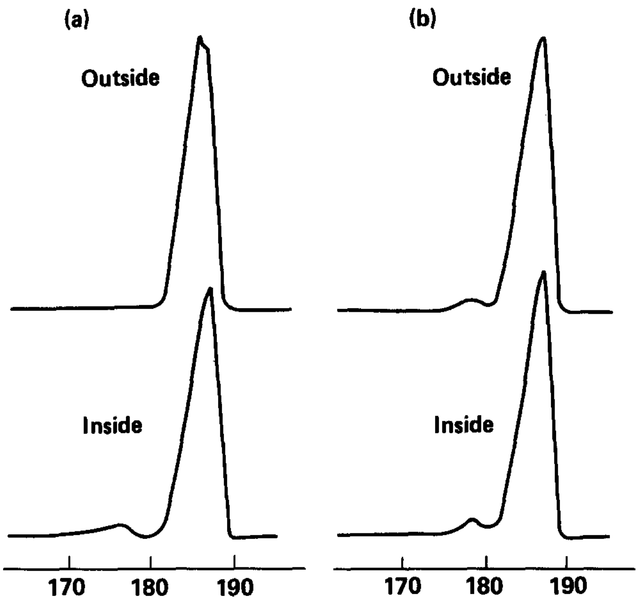

Figure 6 D.s.c. melting endotherms of drawn samples. Precursor tube: 4 mm diameter. (a) Tensile load 12 kg, $\lambda = 28$; (b) tensile load 21.5 kg, $\lambda = 26$

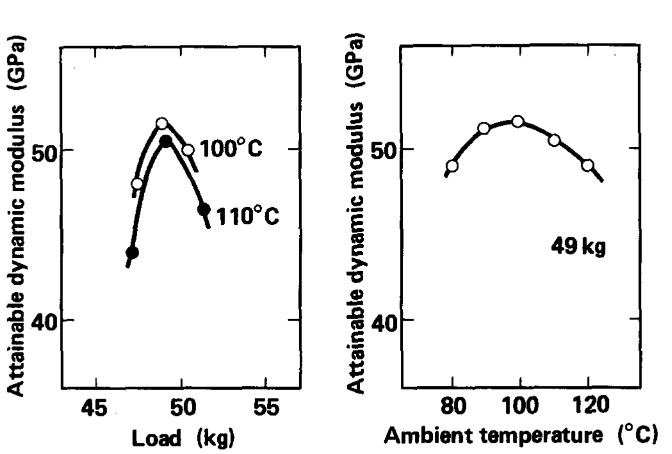

Figure 7 Attainable dynamic modulus *versus* tensile load and ambient temperature for tubes of 6 mm diameter

Influence of precursor size

The drawing behaviour of tubes with outer diameters of 3 mm and 6 mm was investigated. In order to determine the optimum conditions, drawing experiments were performed at different tensile loads and ambient temperatures. As an example, the results on the 6 mm tubes are shown in *Figure 7*. In the figure, the ambient temperature refers to the ambient temperatures of heaters No. 4 through No. 7 in the rear furnace. The ambient temperatures of No. 2 and No. 3 were adjusted to give a maximum dynamic modulus at a given tensile load and at a given ambient temperature. The ambient temperature (No. 1) of the front furnace was kept at 30°C. A maximum dynamic modulus of 51 GPa was obtained at a tensile load of 49 kg and at an ambient temperature of 100°C. The optimum drawing conditions for the different tubes are summarized in *Table 2*. The outer diameter changes in the furnaces, under the optimum drawing conditions for the different size tubes, are shown in *Figure 8*. It has been shown that the sample is drawn at a constant strain rate under the optimum drawing conditions in the ultra-drawing process[4]. In this case, the diameter can be calculated in the process and the strain rate can be evaluated. The calculated diameters are shown with broken curves in *Figure 8*. The observed diameter changes agree well with the calculated curves. From these curves the strain rates were evaluated for the different size tubes.

The precursor size dependences of the optimum drawing conditions and the attainable values are summarized in *Figure 9*. The optimum drawing conditions and the attainable values depend strongly on the precursor size. The attainable dynamic modulus

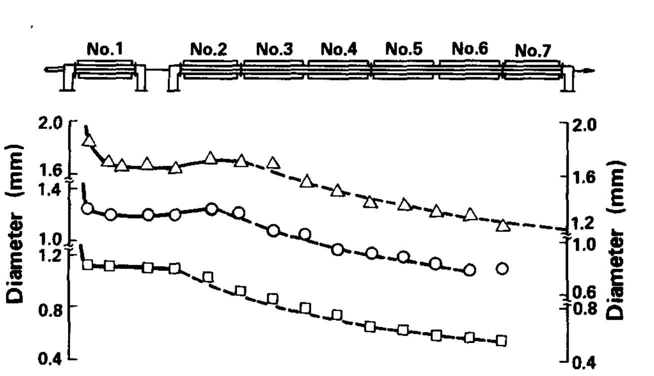

Figure 8 Drawn sample diameter changes in the furnaces under optimum drawing conditions. Precursor tube size: 6 mm diameter (△); 4 mm diameter (○); 3 mm diameter (□). Drawing conditions are summarized in *Table 2*. Broken curves: calculated diameter changes

Table 2 Optimum drawing conditions for different size tubes

Diameter (mm)		Load	Output (kW)		Ambient temperature (°C)							Maximum	Dynamic
Outer	Inner	(kg)	Front	Rear	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	draw ratio	modulus (GPa)
3	1	8.5	1.0	0.6	30	90	120	130	130	130	130	35	59
4	1	19	0.8	0.4	30	110	120	120	120	120	120	29	54
6	1	49	0.6	0.35	30	130	110	100	100	100	100	29	51

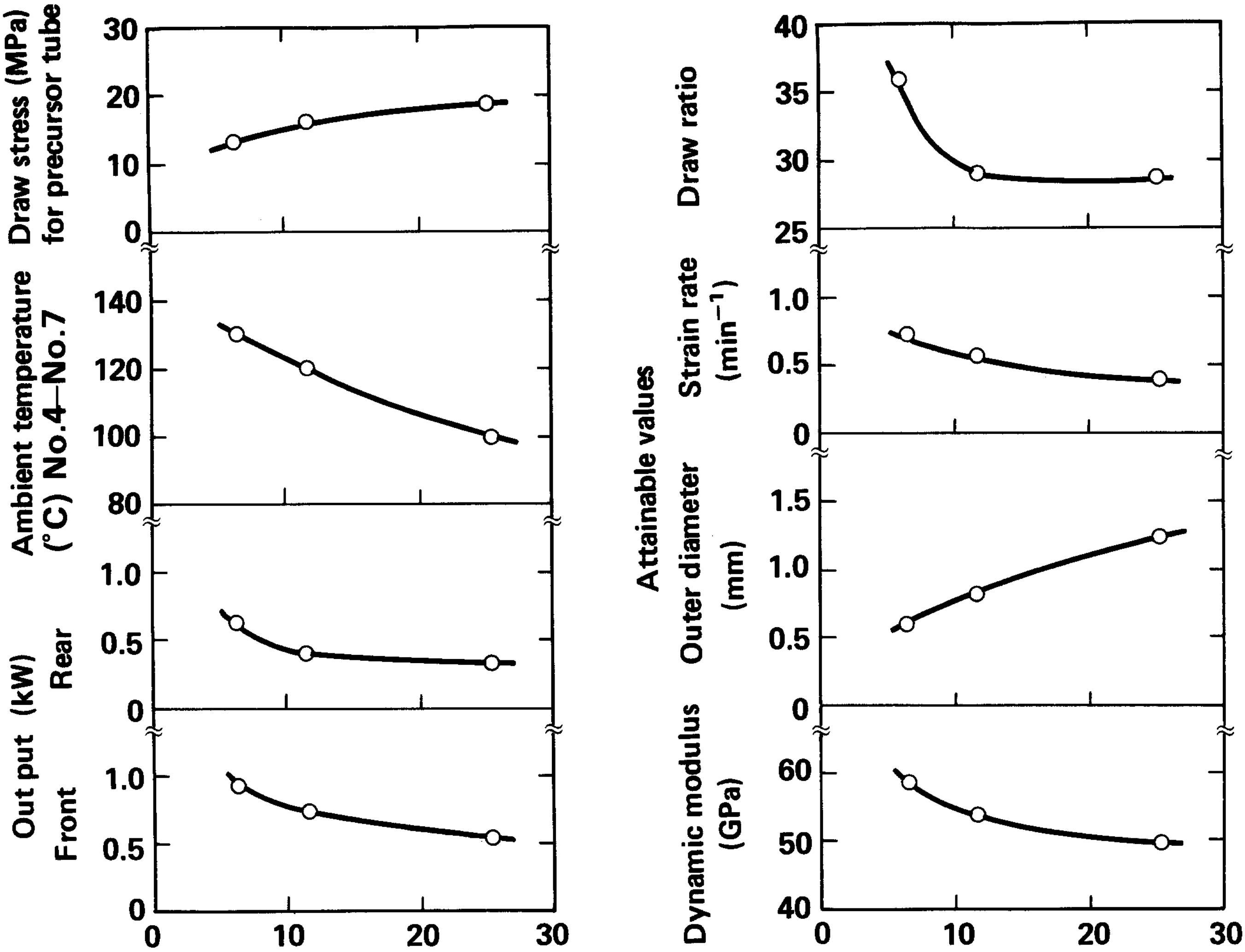

Figure 9 Precursor size dependences of optimum drawing conditions and attainable values

increases with decrease in the cross-sectional area of the precursor tube. The highest dynamic modulus, of 59 GPa, was obtained for tubes of 3 mm diameter at a draw ratio of 35. Although the attainable dynamic modulus was 51 GPa for 6 mm diameter tubes, drawn samples with diameters greater than 1 mm can be compared with glass-fibre reinforced plastic rods. The reduction of the attainable dynamic modulus, draw ratio and strain rate with increase in the precursor size is due to the drawing conditions.

In order to compare the optimum tensile loads for different tubes, the draw stresses were calculated. The draw stress was defined as tensile load per cross-sectional area of the precursor tube. The optimum draw stress increased from 14 MPa to 19 MPa as the precursor size increased in cross-sectional area from 6 mm^2 to 25 mm^2, as shown in *Figure 9*. This means that the sample temperature decreased with increase in the precursor size. In fact, the ambient temperatures of No. 4 through No. 7. and the microwave outputs were depressed with increase in the precursor size. It seems that the reduction of attainable values in dynamic modulus, draw ratio and strain rate with increase in the precursor size is, more precisely, due to the depression of the sample temperature.

The melting endotherms of samples prepared by drawing 6 mm diameter tubes under the optimum tensile load of 49 kg are shown in *Figure 10*. Additional, small melting peaks were observed slightly below the main peak. These melting endotherms are similar to those of samples prepared by drawing 4 mm diameter tubes under the highest tensile load of 21.5 kg, as shown in *Figure 5e*. The occurrence of the subpeaks may be due to the melting of small crystallites, which partially remained in the POM because of the low sample temperature.

It may be necessary to depress the draw stress in order to obtain the highest dynamic modulus of 59 GPa (which was attained for 3 mm diameter tubes) for wider tubes (such as 4 mm and 6 mm diameter tubes). For example, the draw stress of 14 MPa for 3 mm diameter tubes corresponds to a tensile load of 16 kg for 4 mm diameter tubes and that of 36 kg for 6 mm diameter tubes. However, the highest dynamic moduli were not obtained at these lower tensile loads, as shown in *Figures 2* and *7*. In particular, for 6 mm diameter tubes, the drawing experiments could not be made at such a low tensile load because runaway heating, which is one of the features of microwave heating, occurred in the rear furnace. In microwave heating, the centre of the sample is inclined to heat more intensely, as shown in *Figure 6a*. This tendency

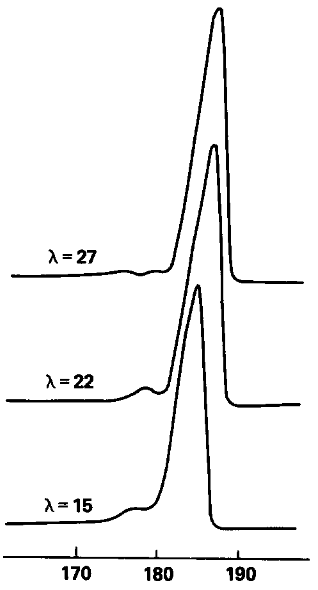

Figure 10 D.s.c. melting endotherms of drawn samples. Precursor tube of 6 mm diameter and optimum tensile load of 49 kg

is enhanced with increase in the cross-sectional area. Also, the excess heating in the inner section is amplified in the long furnace. This weak point of microwave heating may be overcome by dividing the rear long furnace into several short furnaces and independently controlling their outputs.

CONCLUSIONS

In the microwave heat-drawing process, there is an optimum tensile load for high modulus and high strength over all the draw ratios for a given precursor size. For example, the highest values in dynamic modulus and tensile strength were obtained at a tensile load of 19 kg for 4 mm diameter tubes. At lower tensile loads, corresponding to higher sample temperatures, excess heating in the centre of the sample occurs. On the other hand, at higher tensile loads, the sample temperature was too low to rearrange the molecular chains into extended chains in the crystallites.

The optimum drawing conditions depend strongly on precursor size. With increase in the cross-sectional area of the precursor tube, the optimum draw stress increases, i.e. the sample temperature decreases. The depression of the sample temperature causes a reduction of attainable values in dynamic modulus, draw ratio and strain rate. The excess heating in the centre of the sample, due to microwave heating, is enhanced with increase in the cross-sectional area. This excess heating limits the drawing of wider tubes at lower draw stresses.

REFERENCES

1 Nakagawa, K., Maeda, O. and Yamakawa, S. *J. Polym. Sci., Polym. Lett. Edn.* 1983, **21**, 933
2 Nakagawa, K., Konaka, T. and Yamakawa, S. *Polymer* 1985, **26**, 84
3 Konaka, T., Nakagawa, K. and Yamakawa, S. *Polymer* 1985, **26**, 462
4 Nakagawa, K. and Konaka, T. *Polymer* 1986, **27**, 1030
5 Clark, E. S. and Scott, L. S. *Polym. Eng. Sci.* 1974, **14**, 682
6 Brew, B. and Ward, I. M. *Polymer* 1978, **19**, 1338
7 Coates, P. D. and Ward, I. M. *J. Polym. Sci., Polym. Phys. Edn.* 1978, **16**, 2031
8 Hope, P. S., Richardson, A. and Ward, I. M. *J. Appl. Polym.Sci.* 1981, **26**, 2879