Production of high-modulus poly(ethylene terephthalate) rods by a microwave heat-drawing technique

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High-modulus poly(ethylene terephthalate) (PET) rods were produced by a microwave heat-drawing technique. The drawing conditions to yield the maximum modulus were examined. The dynamic modulus (3.5 Hz) reached 24.9 GPa under an appropriate drawing condition. The orientations of the drawn rods were transversely uniform at every draw ratio. It was shown that microwave heating for drawing PET was not as effective as for drawing polyoxymethylene (POM), because the maximum modulus of microwave-drawn PET rods exceeded that of conventionally-drawn ones by only about 10% (50% enhancement for microwave-drawn POM). The continuous production of high-modulus PET rods was possible at a rate of 1.7 m min^{-1} to yield 25 GPa.

(Keywords: poly(ethylene terephthalate); microwave heating; drawing; dynamic modulus; continuous production)

INTRODUCTION

Poly(ethylene terephthalate) (PET) is a commercially available thermoplastic widely used for textile fibres, films and bottles. Both the mechanical and structural aspects of the drawing behaviour of PET have been extensively studied for many years. It is of interest from scientific and industrial points of view to develop new processing conditions for high-modulus and high-strength PET.

A high-modulus PET fibre with a Young's modulus of 19.4 GPa was prepared by Kunugi *et al.*[1] using their zone annealing method, and its mechanical and structural properties were also studied[2]. Porter *et al.* applied a solid-state co-extrusion method to PET[3,4]. Some properties of co-extruded PET have been studied extensively by several workers[5-8].

Recently, a new processing method, 'microwave heat-drawing', was developed for high-modulus and high-strength polyoxymethylene (POM)[10,11]. By using this method, the Young's modulus and the strength of drawn POM tubes reached 63 GPa and 1.7 GPa, respectively[12]. Tensile modulus of POM by the conventional method was reported by Ward *et al.*[9] to be 39.5 GPa. The modulus yielded by the microwave heat-drawing method exceeded Ward's value by 50%. This can be explained by the selective heating of non-crystalline regions by microwaves. Some mechanical and orientation properties of microwave-drawn POM have also been reported[13,14].

In this paper, high-modulus PET rods were produced by the microwave heat-drawing method, and the optimum drawing conditions were studied to obtain the maximum modulus. Under suitable conditions, high-modulus PET rods were continuously produced.

EXPERIMENTAL

Material

The material used in this study was a commercially available PET (Dianite AA-160, Mitubishi Rayon Co. Ltd). The inherent viscosity was 0.97 dl g^{-1}. Rods of 4 mm and 2 mm diameter were prepared from pellets by extrusion. The density and the birefringence of these rods were 1.34 g cm^{-3} and 0.025 respectively.

Drawing apparatus

The apparatus for drawing used in this study is shown in *Figure 1*. The rod was sent to the microwave heating oven connected to the microwave power source (2.45 GHz, 1.5 kW) by the feeder at a constant speed. The oven was equipped with electric heaters to control the temperature inside. The rod was drawn by the take-up machine. The take-up speed was adjusted to apply a constant tension to the rod. The drawing tension was monitored with the tension monitor. When the sample rods were provided to this apparatus at a desired speed, they were continuously drawn under desired conditions of temperature, tension and microwave power.

Drawing procedure

High tension is necessary to draw the PET rods over their natural draw ratio to get high moduli. However, the rods often break at their necks. In this study, to apply a sufficient tension for ultradrawing, drawing was performed in the following two steps: (1) drawing to make the specimen strong enough in the next drawing; (2) subsequent ultradrawing under high tension.

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In order to discover the optimum condition, rods (4 mm in diameter) with a given length were drawn at various temperatures and tensions using the apparatus shown in *Figure 1*. In this case, the feeder was used for sustaining the specimen during drawing; thus the feeding speed was set to zero and tension was adjusted by the take-up machine. The microwave heating oven used here was 1 m long. Pre-drawn rods (drawn (×4) under a tension of 19 kg) were subjected to ultradrawing, where the samples were drawn to draw ratios as high as possible.

Continuous production of ultradrawn PET rods was performed using a 5 m long microwave heating oven by taking into consideration the optimum condition obtained in the drawing shown above. Rods of 2 mm and 4 mm diameter were used. These rods were pre-drawn to a draw ratio of 4 under a tension of 19 kg, and then subjected to ultradrawing by microwave heating. The feeding speed was adjusted to 0.80 m min^{-1} to produce drawn rods at a rate of more than 1 m min^{-1}.

Measurements

The densities of the samples were measured by a flotation method using n-hexane/carbon tetrachloride mixtures. The degree of crystallinity was calculated from the density, using the crystal density[15] of 1.455 g cm^{-3} and the amorphous density[15] of 1.335 g cm^{-3}.

The dynamic moduli of drawn rods were measured at 3.5 Hz with a Rheovibron DDV-3-EA (Toyo Baldwin Co. Ltd). The sample length and the amplitude were 70 mm and $\pm 25\,\mu m$, respectively. The cross-sectional areas of the rods were determined from the weight per unit length using the measured densities. Draw ratios were determined from the ratios of the cross-sectional areas before and after drawing.

Birefringence (Δn) was determined from the retardation (R) measured with a polarized microscope XTP-11 (Nicon Co. Ltd) for specimens with a microtome, using the following equation

$$\Delta n = R/d$$

where d is the sample thickness.

RESULTS AND DISCUSSION

Microwave heat-drawing

Dynamic moduli obtained by the conventional drawing method (without using microwave power) were compared with those by microwave heat-drawing. For both methods, various conditions were examined to yield the maximum modulus. As for the conventional drawing, the dynamic modulus depends on two parameters, i.e. applied tension and oven temperature. The tension dependence of the modulus at a draw temperature of 190°C is shown in *Figure 2*. There is a suitable tension around 50 kg for obtaining the maximum modulus. Tension to yield maximum modulus at each temperature was examined between 160°C and 210°C. These maximum moduli and their corresponding draw ratios are shown in *Figures 3* and *4*, respectively, with open circles.

For microwave heat-drawing, microwave power was adjusted to yield a maximum modulus under a given temperature and tension. In *Figures 3* and *4*, the maximum moduli and the corresponding draw ratios over the temperature range of 120°C to 160°C are shown, respectively, with closed circles. The tension applied here was 45 kg, which was the suitable tension for 140°C. The conditions yielding maximum moduli are summarized in *Table 1*. The dynamic modulus of 24.9 GPa by the microwave heat-drawing method exceeds the value for high-tenacity filament prepared by the conventional method. The draw ratio dependence of dynamic moduli is shown in *Figure 5*. The dynamic modulus increases with the increase in draw ratio, and the highest value of 24.9 GPa was obtained at a draw ratio of 8.7×.

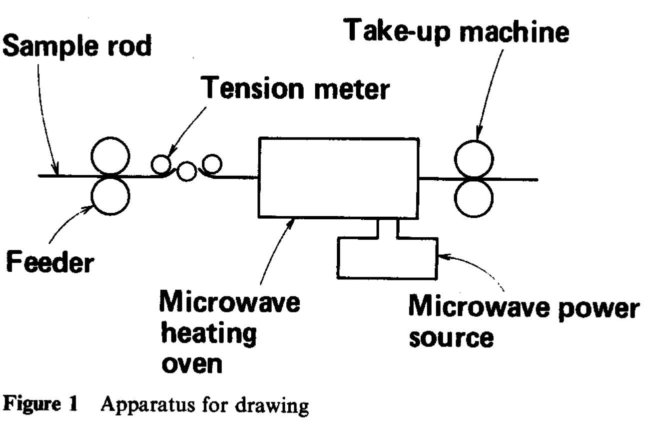


Figure 1 Apparatus for drawing

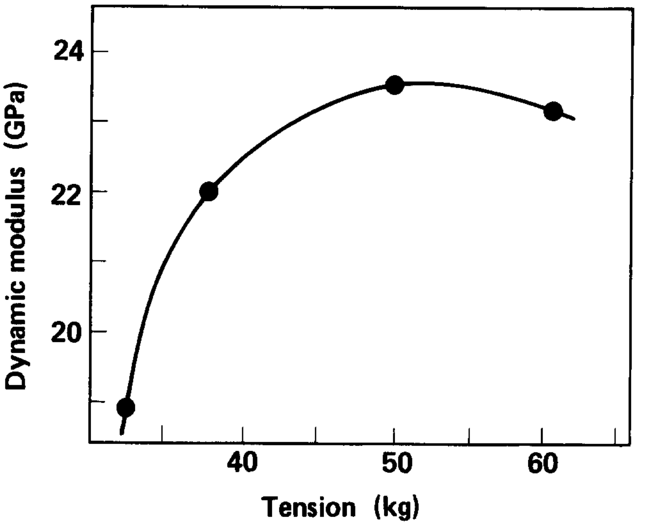


Figure 2 Relationship between dynamic modulus and applied tension

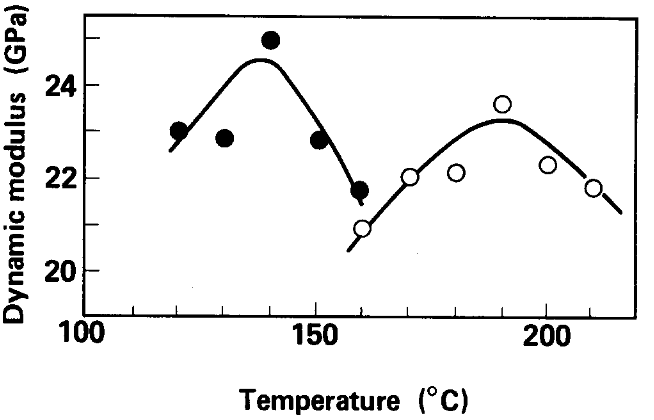
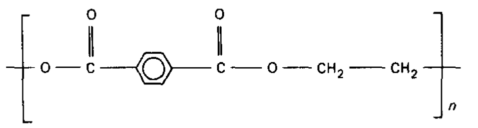


Figure 3 Relationship between oven temperature and dynamic modulus: microwave heat-drawing (●); conventional drawing (○)

However, the difference between the moduli obtained by these two methods is only about 1 GPa. The microwave heating effect for PET is small compared with that for POM, of which the modulus was 50% larger compared with the highest value obtained by the conventional method. This may be attributed to the following reasons.

(1) Low mobility of PET molecules: PET has the following molecular structure.



The benzene ring is bulky and hinders the molecular movement for the orientation during drawing. Therefore, molecular mobility induced by heating and tension is insufficient for the extension and orientation of entangled molecules.

(2) Lower crystallinity of PET compared with POM: The crystallinity of PET, estimated from the density, was 60% for a draw ratio 8× (see *Figure 6*), while that of POM was between 70% and 90%. It is considered that, although the amorphous regions are selectively heated by microwaves, the generated heat is excessive for the selective heating of the amorphous regions because of the low crystallinity of PET. This causes heating of the crystalline region, resulting in a uniform temperature for both regions, as is the case with conventional drawing. In the case of POM, it is thought that the molecular motion of non-crystalline (amorphous and crystal defect) regions is selectively excited by microwaves and POM can be effectively drawn without disordering the oriented crystalline regions because of the high crystallinity.

Therefore, high molecular mobility and high crystallinity are necessary for yielding higher moduli by microwave heat-drawing.

Birefringence measurements

The inside of the drawn rods was fibrillized when the draw ratio reached around 7×. However, the surface was smooth and not fibrillized. Birefringence in its sectional area was measured to examine the uniformity of the transverse orientation of drawn rods. The variation of birefringence in the cross section of drawn samples is shown in *Figure 7*. The birefringence did not change transversely in any draw ratio except for a drawn sample in which the necking occurred at room temperature. This sample was a two-layered structure in the transverse direction, where the inner layer was whitened. The birefringence of this sample designated with open circles in *Figure 7*, increases as the distance from the centre increases. Konaka *et al.*[12] reported that the non-uniformity of birefringence in the cross section was observed for highly drawn POM. They proposed that non-uniformity of heating occurred during drawing. In the present study, the non-uniformity of birefringence is thought to occur for the same reason. When samples were drawn in appropriate conditions, however, the orientation was transversely uniform.

Continuous drawing

The oven temperature and the applied tension were examined around 140°C and 45 kg, respectively,

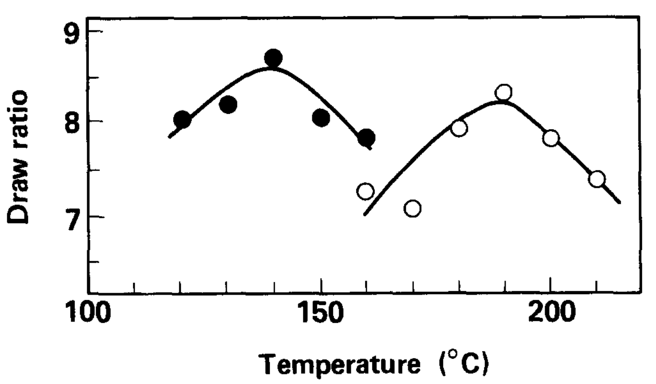


Figure 4 Relationship between oven temperature and draw ratio: microwave heat-drawing (●); conventional drawing (○)

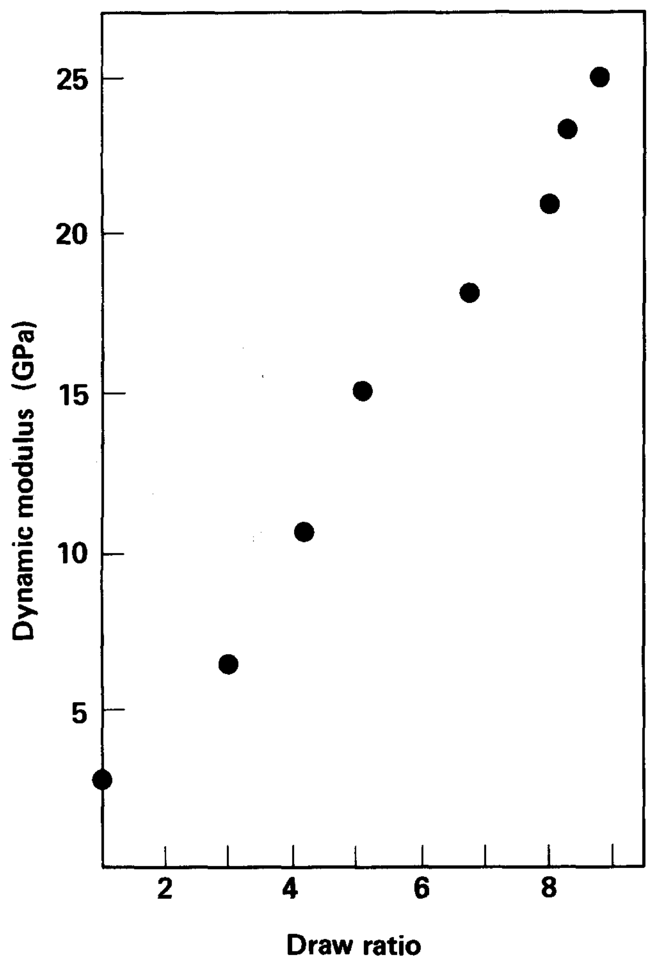


Figure 5 Dynamic modulus vs. draw ratio

Table 1 Drawing conditions for maximum moduli

Method	Tension (kg)	Temperature (°C)	Modulus (GPa)	Draw ratio	Diameter (mm)
Conventional	50	190	23.5	8.3	1.39
Microwave heating	45	140	24.9	8.7	1.36

Table 2 Conditions for continuous drawing

Diameter (mm) (undrawn)	Temperature (°C)	Take-up speed (m min^{-1})	Modulus (GPa)	Diameter (mm) (drawn)	Draw ratio
4	140	1.7	25	1.4	8.2
2	160	1.3	25	0.7	8.2

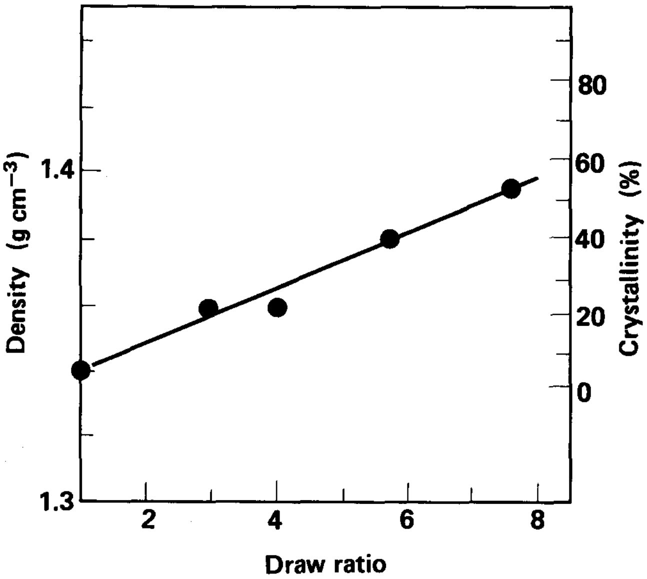


Figure 6 Density vs. draw ratio

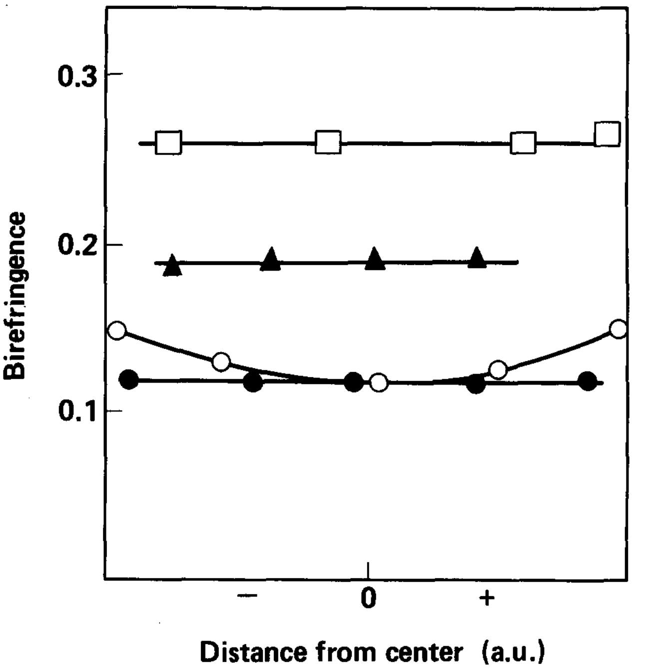


Figure 7 Variation of birefringence across the width of samples drawn to the draw ratio of 3 (●), 4 (▲) and 7.6 (□). A sample for which the neck was formed at room temperature is also shown (○)

according to the conditions for yielding the maximum modulus. The microwave power was adjusted to attain the maximum draw ratio and modulus at each temperature and tension. The continuous drawing conditions for maximum moduli are shown in *Table 2*. The dynamic moduli of both rods (2 mm and 4 mm diameter) attained 25 GPa, which is comparable with the maximum modulus shown in *Table 1*. The production rate was 1.7 m min^{-1}. The moduli attained were independent of the diameters of the original rods. The applied tension for the 4 mm rods was set at 40 kg, which was lower than the suitable value (45 kg) of *Table 1*, to prevent the rod from breaking during continuous production. The suitable oven temperature for the 2 mm wide rods was 160°C, which was higher than the value shown in *Table 1*, since the sample volume to absorb the microwave energy was smaller than that of the 4 mm wide rods and the heat generated was lower.

CONCLUSION

Rods of PET were drawn by the microwave heat-drawing method to obtain 25 GPa for the maximum modulus. This value exceeds previously reported values and is the highest modulus obtained for PET rods. The suitable condition yielding the maximum modulus was an applied tension of 45 kg and an oven temperature of 140°C. A uniform orientation in the transverse direction was confirmed by birefringence measurements. However, the microwave heating effect was not so obvious as in the case of POM. This was thought to be due to the low crystallinity and the low molecular mobility of PET. Continuous production of high-modulus drawn PET rods was performed at a production rate of 1.7 m min^{-1} to obtain 25 GPa for the modulus.

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