

Preparation of Ultra-High Modulus Polyvinyl Alcohol Fibers by the Zone-Drawing Method

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Synopsis

The zone-drawing method has been applied to prepare ultra-high modulus polyvinyl alcohol fibers. First, the suitable temperature for zone-drawing was decided. In the first zone drawing, when drawing temperature was as high as near melting point, the highest draw ratio and modulus were obtained. The modulus was further increased by repeating zone drawing and heat treatment. In this study, the highest dynamic moduli were 115 GPa at room temperature and 42 GPa at 200°C. The fiber has a sharp melting peak that appeared at 246°C and a small peak at 260°C in the DSC curve.

INTRODUCTION

Molecular chains of polyvinyl alcohol in the crystal take a zig-zag conformation like those of polyethylene. Because C—C bonds have a high bond energy, the crystal modulus¹ is so high, which is estimated as 250–300 GPa being comparable to polyethylene crystal modulus. However, the maximum modulus attained so far has not exceeded 60 GPa in spite of various attempts^{2–5} for polymerization control, gel spinning, and drawing. It is necessary to reconsider the reasons. The differences in structure between polyvinyl alcohol and polyethylene are the existence of the OH group and the hardness of the crystals. The OH groups cause steric hindrance and prevent slippages and alignments of molecular chains during drawing or annealing. In addition, hydrogen bonds are formed between adjacent OH groups. The intra- or intermolecular hydrogen bonds are very numerous and random in orientation,⁶ compared with hydrogen bonds in nylon 6. On the other hand, the crystal of polyvinyl alcohol has a much higher melting point of 228–250°C than that of polyethylene, which is 125°C, and is harder in plastic deformation. The crystals act as points that bundle the molecular chains and inhibit the free movement of amorphous chains.

From such reasons, we have considered that the hydrogen bonds and hard crystals rather than molecular chain entanglements, which have been discussed with attention for polyethylene, are more important for superdrawing of polyvinyl alcohol. Unless the hydrogen bonds and crystals are dissolved or softened, the superdrawing comparable to that of polyethylene will be impossible.

In the present study, the zone-drawing method^{7–17} has been employed in order to resolve these problems.

EXPERIMENTAL

Material

The original material is as-spun polyvinyl alcohol fibers with a high polymerization degree of 11,800, a crystallinity of 44%, a saponification value of 99.9%, and a diameter of 184 μm , which was supplied by KURARE Co., Ltd.

Zone Drawing and Vibrational Heat Treatment

Zone drawing was carried out by moving a narrow heater along the original fiber under a suitable tension. The temperature and tension were selected so that the necking part of the fibers was located in the heating zone. In this study, the heater temperature on drawing (T_d) was varied from 80 to 260°C under a constant tension of 1.7 kg/mm². For parts of the zone-drawn fibers, zone drawing was repeated two or three times, under more severe conditions, and finally vibrational heat treatment was tried at 110 Hz. After zone drawing or heat treatment, draw ratios were calculated from changes in length.

Measurements

The birefringence was measured with a polarizing microscope equipped with a Berek compensator. DSC curves, X-ray equatorial diffraction patterns, and WAXS photographs were obtained for fibers at each stage.

The dynamic viscoelasticities, E' and E'' , were measured at 110 Hz and at a heating rate of 2.7°C/min from 0 to about 230°C with a dynamic viscoelastometer, VIBRON DDV-II (Orientec Co. Ltd.). The tensile tests were carried out at 23–25°C and RH 65% on the fibers of about 30 mm in gauge length and at a crosshead speed of 10 mm/min, using a tensile tester, TENSILON II (Orientec Co. Ltd.). The tensile modulus, strength, and elongation at break were evaluated from the strain–stress curves.

RESULTS AND DISCUSSION

Effects of Drawing Temperature on Superstructure and Mechanical Properties of the Drawn Fibers

In order to elucidate on the effects of zone-drawing temperature (T_d) on the superstructure and mechanical properties, the zone drawing (ZD) was carried out at heater temperatures between 80 and 260°C at 5 or 10°C intervals under a constant tension of 1.7 kg/mm², total experiments being 47 times.

Figure 1 shows the relation between T_d and draw ratio. The draw ratio was discontinuously increased around 90°C. This temperature corresponds to the glass transition temperature (T_g) of this polymer. The draw ratio increased rapidly above 200°C and reached 15-fold. However, the fibers were breaking at T_d above 260°C.

Figure 2 shows the change in birefringence with T_d . The birefringence increased gradually in the T_d range of 100–260°C. The maximum value is 56×10^{-3} , which is higher than the intrinsic birefringences of crystal and amorphous phases of 51.8×10^{-3} and 43.8×10^{-3} proposed by Kawai et al.¹⁸

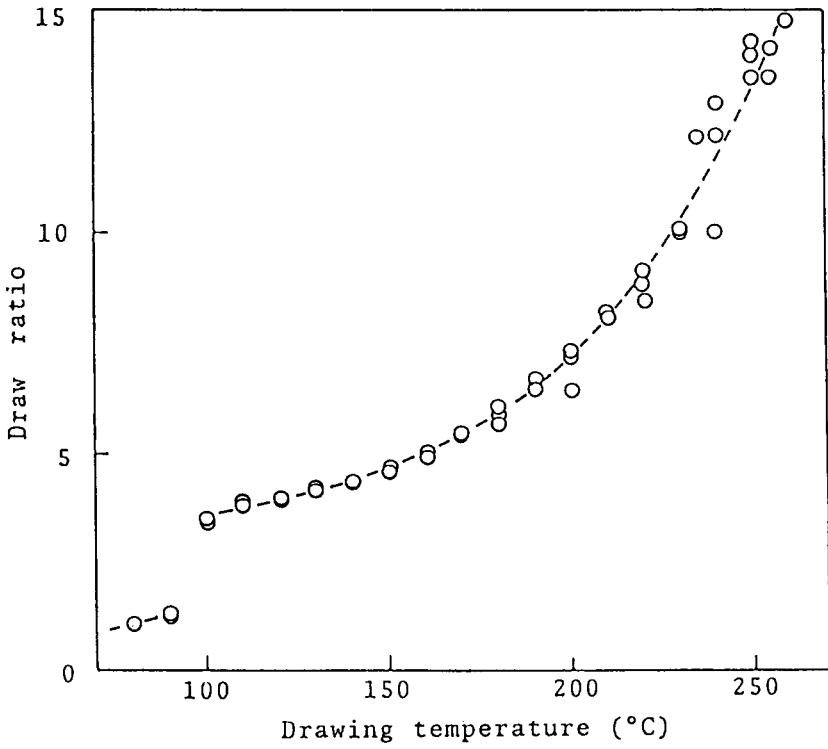


Fig. 1. Relation between the draw ratio and drawing temperature.

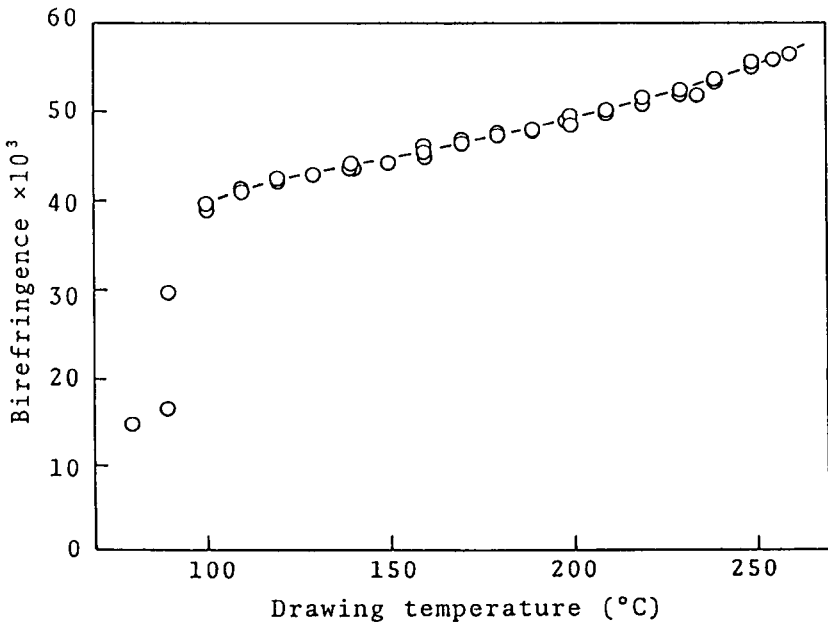
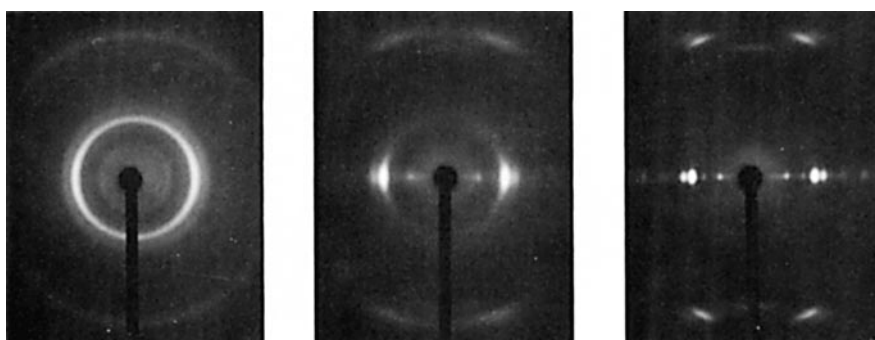


Fig. 2. Relation between the birefringence and drawing temperature.



Original fiber

Fiber zone-drawn at 100°C

Fiber zone-drawn at 180°C

Fig. 3. Wide-angle X-ray diffraction photographs for the original fiber, the fibers zone drawn at 100 and 180°C.

Figure 3 shows wide-angle X-ray photographs of the original fiber, the fibers zone-annealed at 100 and 180°C. It is clear that the crystallites can attain a fairly high level orientation even by zone drawing at 100°C. The fibers zone drawn at T_d of 120–260°C indicate X-ray photographs similar to that of the fiber zone drawn at 180°C. The crystal orientation seems to be almost not affected by T_d .

Figures 4–6 show the effect of T_d on Young's modulus, tensile strength, and elongation at break. Young's modulus and tensile strength were rapidly in-

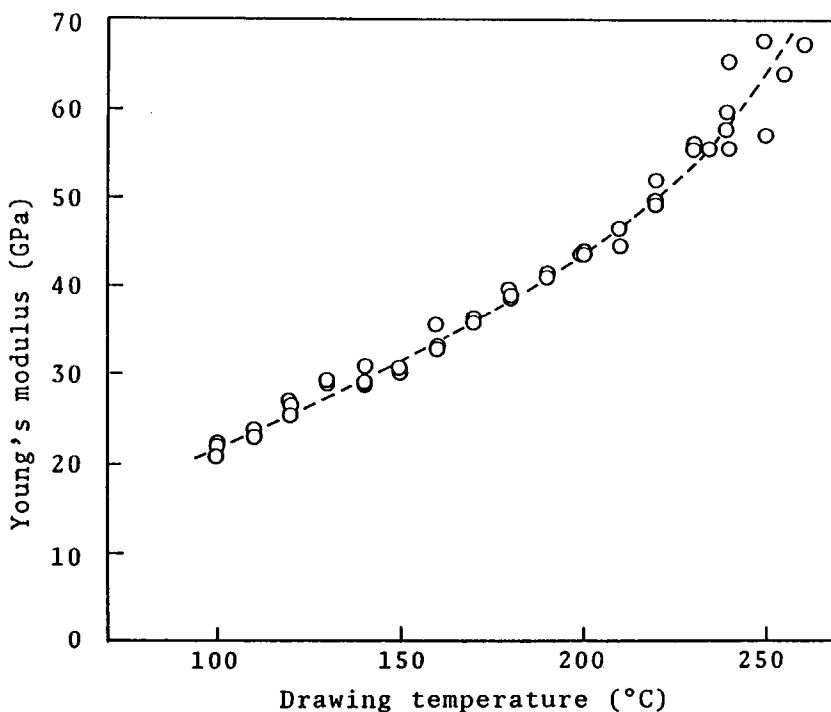


Fig. 4. Relation between the Young's modulus and drawing temperature.

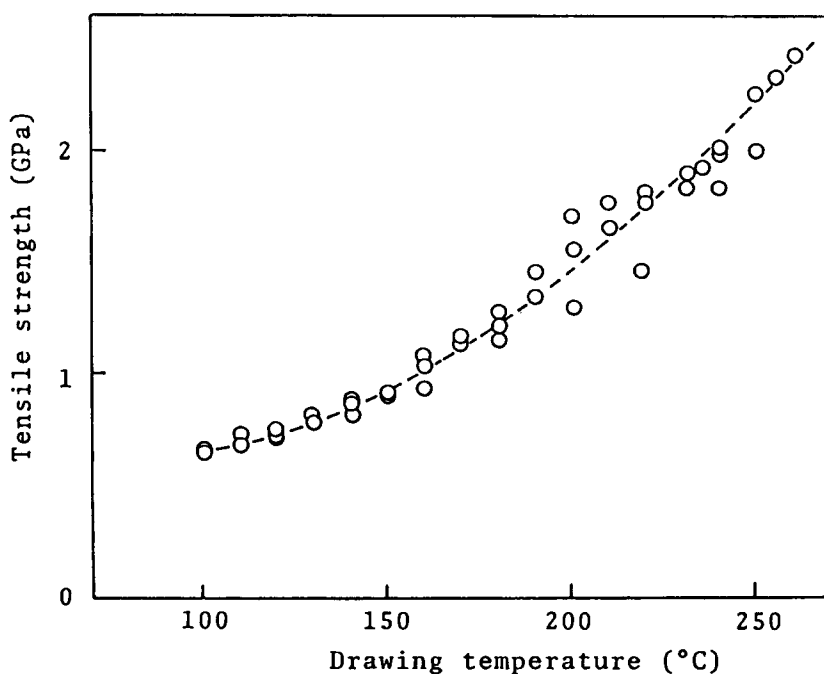


Fig. 5. Relation between the tensile strength and drawing temperature.

creased with increasing T_d , particularly in the higher T_d range. Young's modulus and tensile strength reached 70 GPa and 2.4 GPa, respectively.

Figure 7 shows the temperature dependence of dynamic modulus E' as a function of T_d . The E' value was increased over a whole temperature range measured with increasing T_d . Particularly above 220°C, the increments of E' became larger in spite of the same T_d interval of 20°C. This tendency is similar to those seen in Young's modulus and tensile strength. The maximum E' at room temperature is 90 GPa.

Figure 8 shows the temperature dependence of $\tan \delta$ for the fibers zone drawn at various T_d . The α dispersion peak, which corresponds to T_g , occurred at a constant temperature of 60°C and was not affected by T_d . However, a dispersion peak at higher temperatures, which seems to be the crystalline dispersion, shifted to higher temperature with increasing T_d . It suggests that the crystal structure becomes more rigid as T_d is increased. Figure 9 shows a DSC curve for a fiber zone drawn at a high temperature. It is found that the melting onset temperature is very high and the peak is very sharp. From this fact, it is speculated that the crystalline regions in the fiber are made up of the crystallites with very uniform size and no disorder. The melting point is 246°C. Additionally a small and broad peak appears at 260°C.

In X-ray diffraction patterns for the zone-drawn fibers, well-isolated peaks and very low baselines were observed. This indicates that amorphous contribution to the total X-ray diffraction intensity is very small, namely the degree of crystallinity is appreciably high. The crystallinity was estimated to be 80% from a X-ray pattern. Also, crystallite sizes for (100) and (020) planes were

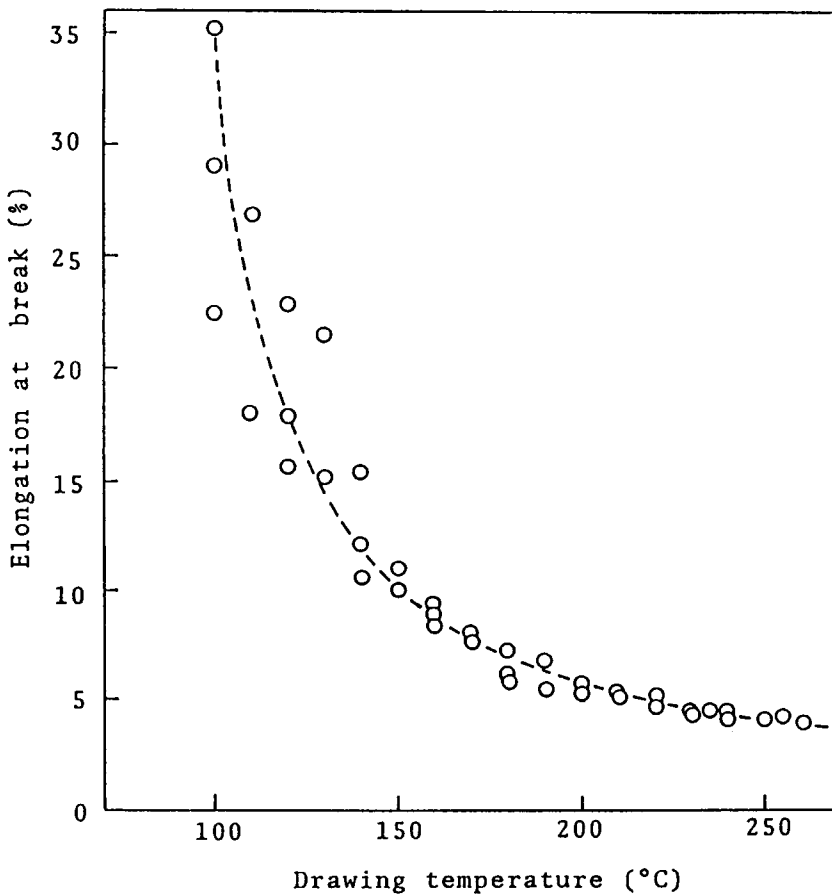


Fig. 6. Relation between the elongation at break and drawing temperature.

calculated to be 68 and 159 Å, by a Kurare research group. It indicates that crystallites are well developed in the longitudinal direction.

High-temperature Zone-drawing Method

As described, when the zone drawing was carried out at a high temperature near the melting point, a high drawability and excellent mechanical properties could be attained. This effect has already been demonstrated for polypropylene films¹⁹⁻²¹ and ultra-high molecular weight polyethylene single-crystal mats.^{16,19,20} The process has been named high-temperature zone-drawing method by us. The principle of the method can be schematically indicated as in Figure 10. In the narrow area heated at a temperature near melting point, the crystallites are fully softened and the molecular chains are easily drawn out by relatively low tension. In the case of polyvinyl alcohol, the hydrogen bonds and rigid crystallites can be simultaneously loosened or destroyed. Then the structure

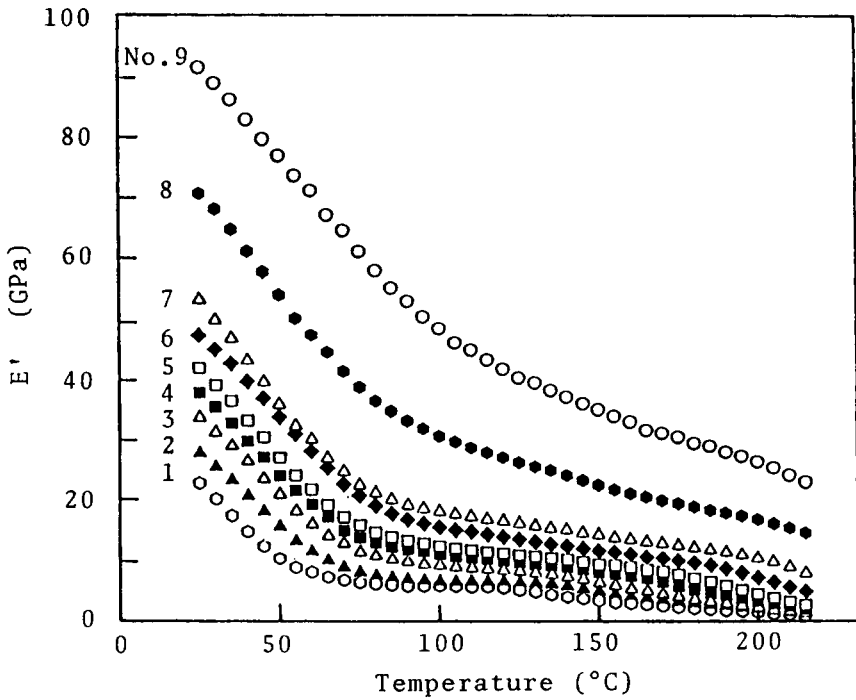


Fig. 7. Temperature dependence of the dynamic modulus for the fibers zone drawn at various drawing temperatures under a same tension of 1.7 kg/mm^2 : No. 1, zone drawn at 100°C ; No. 2, at 120°C ; No. 3, at 140°C ; No. 4, at 160°C ; No. 5, at 180°C ; No. 6, at 200°C ; No. 7, at 220°C ; No. 8, at 240°C ; No. 9, at 260°C .

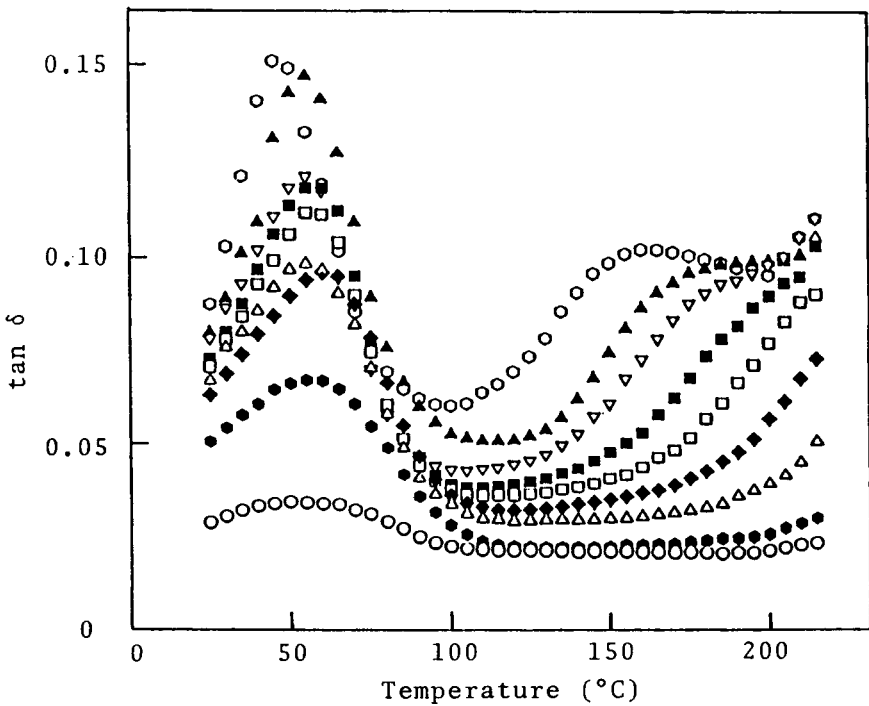


Fig. 8. Temperature dependence of $\tan \delta$ for the fibers zone drawn at various drawing temperatures under a same tension of 1.7 kg/mm^2 : The symbols are as indicated in Figure 7.

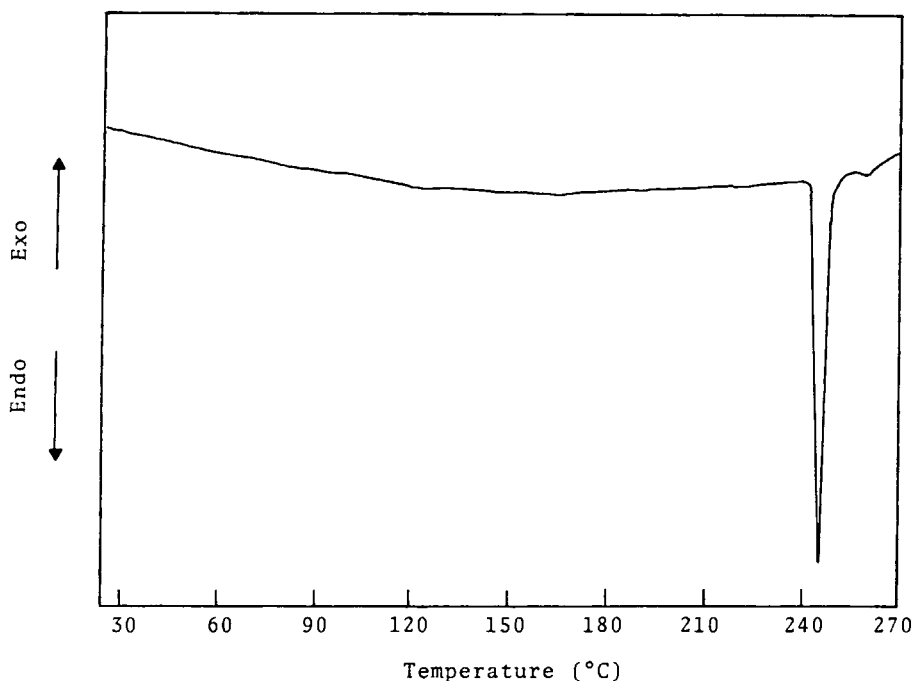


Fig. 9. DSC curve for the fiber zone drawn at 260°C. (The fiber was finely cut and was packed in Al pan; the heating rate was 10°C/min).

of the original fiber may be continuously changed into an extended chain structure by shifting the narrow heating zone along fiber axis.

In the case of this method, the alignment and/or quantity of crystallites in the original material, namely the initial morphology and history of starting materials, do not come into question.

This method has been further tried on other kinds of polymers and interesting results were obtained.

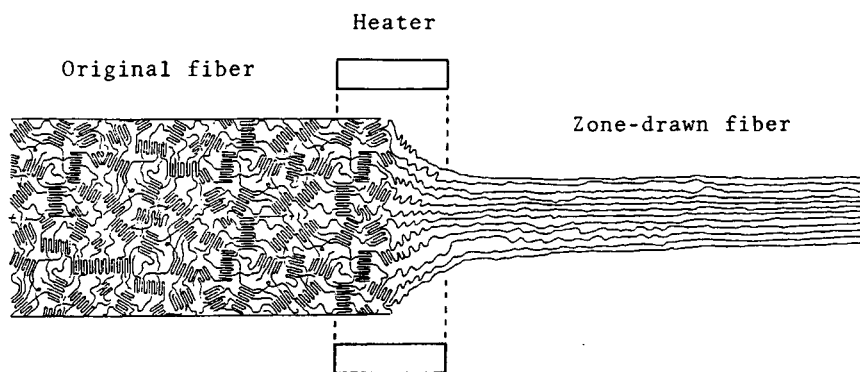


Fig. 10. Principle of the high-temperature zone drawing, which is schematically indicated.

TABLE I
Conditions for Each Zone-Drawing Step and Heat Treatment

	Temperature (°C)	Tension (kg/mm ²)
First ZD	255	1.7
Second ZD	210	25
Third ZD	220	30
Heat treatment	max 230	— (at 110 Hz)

Repeating of Zone-drawing and Vibrational Heat Treatment

Usually, after the first high-temperature zone drawing, the molecular chains are not fully stretched. Then it is necessary to repeat zone drawing and further zone annealing under more severe conditions for improving mechanical properties of the fibers. Tables I and II show the conditions for the first, second, and third zone drawing and then vibrational heat treatment. At the second and third zone drawings, the tension was drastically increased to 25 and 30 kg/mm², although the T_d were 210 and 220°C, which were lower than the T_d at the first zone-drawing, i.e., 255°C. The third zone-drawn fiber was further heat treated from room temperature to 230°C at a heating rate of 3°C/min under a vibration of 110 Hz. Figure 11 shows the temperature dependence of dynamic modulus E' . The E' value increased in order of the processing over the whole temperature range. Fiber No. 13 has a very high dynamic modulus of 115 GPa at 20°C. In addition, the fiber exhibits a high modulus even at elevated temperatures, for example, 50 GPa at 200°C.

Figure 12 shows the temperature dependence of $\tan \delta$ for the same samples as in Figure 11. The α dispersion peak decreased in height and slightly shifted to the higher temperature side with processings. The absolute intensities of the peaks are remarkably lower than those of the first zone-drawn fibers shown in Figure 8. This indicates that the movements of amorphous chains are strongly inhibited. On the other hand, the crystalline dispersion peak could not be observed in Figure 12 because the peak shifted to high temperature with processing. This fact suggests that the crystallites became more perfect and larger. At present, we are investigating in more detail the repetition of zone drawing and its effects. The results will be reported in the near future.

TABLE II
Captions of Sample Numbers in Figure 11

Sample no.	Drawing and vibrational heat treatment
10	First ZD
11	First ZD—second ZD
12	First ZD—second ZD—third ZD
13	First ZD—second ZD—third ZD—heat treatment

CONCLUSION

1. The zone-drawing method was applied to polyvinyl alcohol fiber and was effective in producing high modulus fibers.
2. It was found that the zone-drawing temperatures as high as near the melting point are required for preparing the fibers with excellent mechanical properties.
3. When the zone drawing is repeated, the mechanical properties are further improved. By the combined uses of the multistep zone drawing and vibrational heat treatment, the modulus reached a high level. The highest moduli were 115 GPa at 20°C and 42 GPa at 200°C.
4. The zone-drawn fiber has a sharp melting peak at 246°C in the DSC curve.

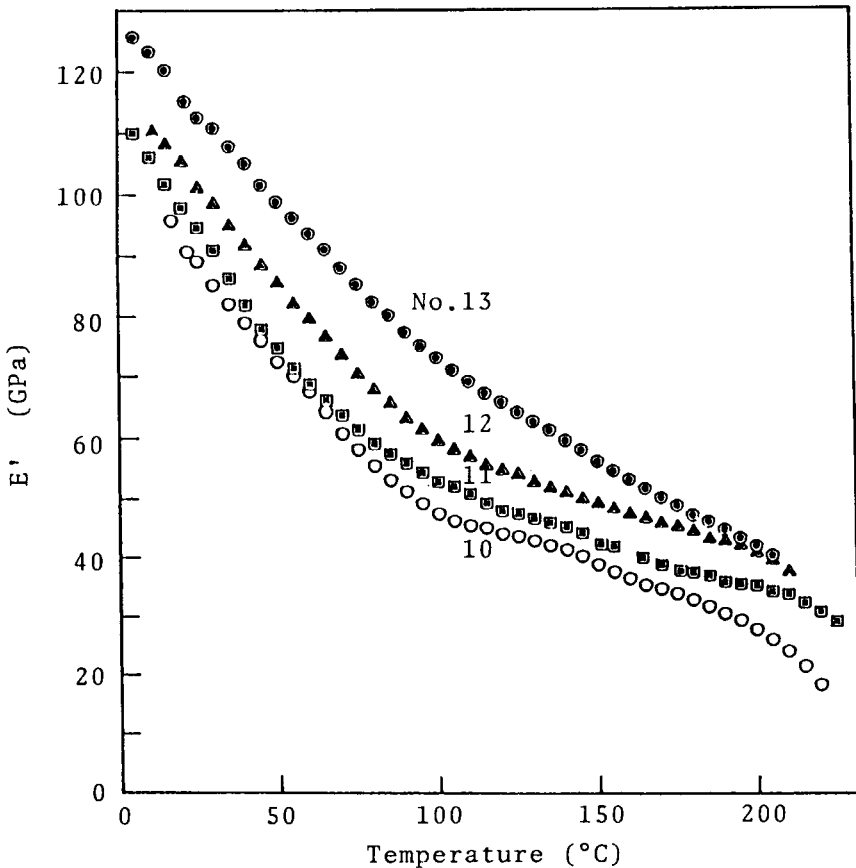


Fig. 11. Temperature dependence of the dynamic modulus for the first, second, and third zone drawn fibers and the three times zone-drawn and vibrationally heart-treated fiber. The conditions for zone drawing and heat treatment are indicated in Tables I and II.

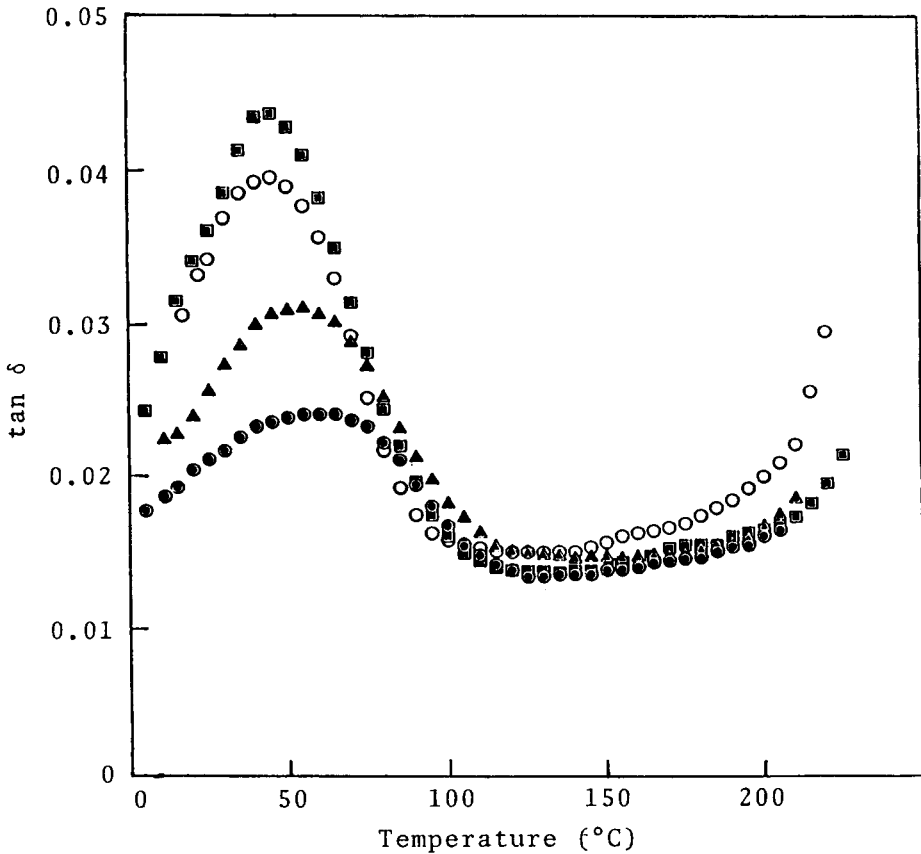


Fig. 12. Temperature dependence of $\tan \delta$ for the first, second, and third zone-drawn fibers, and the three times zone-drawn and vibrationally heat-treated fiber. The symbols are as indicated in Figure 11.

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