

Preparation of High-Modulus and High-Strength Poly(ethylene Terephthalate) Fiber by Zone Annealing

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Synopsis

To prepare high-modulus and high-strength PET fiber, a new method using zone drawing and zone annealing has been studied. The apparatus used for this method is the usual tensile tester equipped with a band heater 2 mm wide and a sample holder which can apply a high tension to the fiber. The experimental procedure consists of two stages: zone drawing and zone annealing. The zone drawing was done on the original as-spun fiber in order to produce a fiber with as high an orientation and as low a crystallinity as possible. The zone-drawn fiber was subsequently zone annealed under high tension by moving the band heater from one end to the other of the fiber at a temperature above the crystallization temperature at a considerably low moving speed. In spite of the simple apparatus and procedure, Young's modulus of the fiber obtained was 19.4×10^{10} dyn/cm², which is comparable to the maximum value of the high-tenacity PET filament commercially available. In order to elucidate the change in the superstructure with zone drawing or zone annealing, optical, x-ray, IR, DSC, and dynamic mechanical measurements were performed. It is suggested that the zone-annealed fiber consists of almost perfectly oriented crystallites and fully extended amorphous chains.

INTRODUCTION

Recently, the preparation of high-modulus and high-strength polymer materials has been studied by many researchers. These studies are roughly divided into two fields: (1) searching for new polymers, and (2) reconstruction of the superstructure of the polymers already widely used. Although the Kevlar fiber¹ developed by du Pont is a well-known example of the former, there are few other commercially produced polymers, in spite of the existence of many synthetic polymers. Because of the many requirements, such as low cost of raw materials, outstanding characteristics, and fully estimated demand, the industrial production of a polymer is very difficult.

On the other hand, the latter is also actively studied and many have been reported: solid-state extrusion,²⁻⁴ crystallization in flowing solution,⁵ high-speed melt spinning,⁶ spinning using liquid crystals,¹ ultradrawing,⁷⁻⁹ freeze spinning,¹⁰ zone drawing,¹¹ crystallization under high pressure,¹² and so on.

This investigation was begun to obtain a fully extended chain crystal. However, it was found that the fiber obtained has excellent mechanical properties in spite of the very simple apparatus and procedure used. The purpose of the present article is to describe a new method of preparation of high-modulus and high-strength fiber, the "Zone-Annealing Method," invented by the authors.¹³

EXPERIMENTAL

Material

The original material used in the present study is as-spun poly(ethylene terephthalate) fiber of diameter about 0.5 mm, supplied by Toray Co. Ltd. The fiber has a birefringence of 0.3×10^{-3} and a crystallinity of 1.8% (from density). Therefore, the fiber can be considered to be nearly unoriented and amorphous.

Zone Drawing and Zone Annealing

The apparatus used for zone drawing and zone annealing is the usual tensile tester partially reconstructed. A band heater 2 mm wide was attached to the crosshead. The temperature of the heater can be held constant throughout the experimental period by a control system. The upper end of the fiber was fixed, and a desired tension was applied to the lower end by weighting. The band heater was moved up or down along the fiber axis, and its moving speed was 2, 4, 8, 10, 20, and 40 mm/min.

The zone drawing was done on the as-spun fiber by moving the band heater from the lower part of the fiber to the upper part while the fiber was held under tension. The fiber was drawn easily and quickly, producing necking. The temperature, the moving speed of the band heater, and the tension were determined so that the drawn fiber had as high an orientation and as low a crystallinity as possible.

The zone-drawn fiber was subsequently zone annealed using the same apparatus as that for the zone drawing, except that three band heaters were superimposed vertically with separation. Both the temperature of the band heater and the tension applied to the fiber during zone annealing were much higher than those in the case of zone drawing. The zone-annealing process was repeated several times at a considerably low speed. Although the heater must be moved upward when the fiber lengthens by zone annealing, there is no effect of the moving direction of the heater if the length of the fiber does not change.

Measurements

The tensile properties of the fibers were determined at 23–25°C, RH ~65%, with a tensile tester, Tensilon UTM-II, SS-105-UTM (Toyo-Baldwin Co., Ltd.). The length of the monofilament used for the measurement was 20 mm. Young's modulus, the tensile strength, and the elongation at break were estimated from the stress-strain curves. The dynamic viscoelastic properties E' , E'' , and $\tan \delta$ were measured at 110 Hz at a heating rate of 1.5°C/min on 20-mm-long fibers over a temperature range from room temperature to ~250°C with a Vibron DDV-II (Toyo-Baldwin Co., Ltd.). The birefringence was measured with a polarizing microscope equipped with Berek's compensator. Because the highly oriented PET fibers have a very high retardation,¹⁴ X-Z planes of various thicknesses which were cut from a single crystal of quartz were simultaneously used as an additional compensator. The density of the fibers was measured at 25°C by a flotation method using toluene-carbon tetrachloride mixtures. The degree of crystallinity was calculated from the density by the usual method using a crystal density¹⁵ of 1.455 and an amorphous region density¹⁵ of 1.335 g/cm³.

Further, IR spectra, DSC curves, wide- and small-angle x-ray photographs, and creep and thermal shrinkage of the fibers were also examined.

RESULTS AND DISCUSSION

Correlation between Fiber Structure and Mechanical Properties

If one wants to obtain a fiber with excellent mechanical properties, first it is necessary to clarify the configuration and aggregation state of the molecules in the fiber and to know in detail the correlation between superstructure and mechanical properties. Peterlin¹⁶ proposed a model for a highly oriented fiber structure, which is generally accepted at present. According to his model, the basic element of the fiber structure is the long and narrow microfibril formed by micronecking of the lamella crystal. The microfibril consists of fully oriented folded chain blocks connected by tie molecules. The microfibrils are bundled into a macrofibril of lateral dimensions of a few thousand angstroms, which is also connected to adjacent macrofibrils by tie molecules.

Because of such an inhomogeneous structure, when force is applied to the fiber, a large stress concentration takes place on the weak elements of the structure, i.e., the tie molecules between macrofibrils or microfibrils and the amorphous layers between the lamellae. In the amorphous layers, there are many end chains and loop chains, but the tie chains carrying the force are very few. Further, these tie molecules have varying lengths and stresses. It is said that the tie molecules transmitting the force represent 2–3% of all the molecular chains in the cross section of the fiber. Therefore, the deformation and fracture¹⁷ of the fiber proceed rapidly through the amorphous regions under high stress. Generally, the strength of fibers is very low compared with the theoretical strength value of the polymer: 1/50–1/100.

Therefore, in order to improve the mechanical properties of the fiber substantially, a fundamental reconstruction of the fiber structure is necessary. As an ideal, the crystalline regions are free from lamellae and consist of extended chain crystals, while the amorphous regions contain a number of the tie molecules passing through many crystals and have a similar extent of stress and length.

Characteristics of the Zone-Annealing Method

Figures 1 and 2 show the principle of this method and a picture of the apparatus used in this study, respectively. As described above, this method consists of two stages: zone drawing and zone annealing. In the first stage, an amorphous (or one with as low a crystallinity as possible) as-spun fiber is converted into a fiber with high orientation and low crystallinity (if possible, amorphous state) by zone drawing at a temperature below the crystallization temperature of the polymer. In the secondary stage, the zone-drawn fiber is further converted into a highly oriented and highly crystalline fiber by zone annealing at the most suitable temperature for crystallization under high tension. In other words, the zone drawing is carried out with the intention of preventing the crystallization of the fiber and of arranging the molecular chains in a bundle. The zone annealing is carried out to inhibit back-folding of the molecular chains by moving the narrow band heater in one direction and to form perfectly extended chain

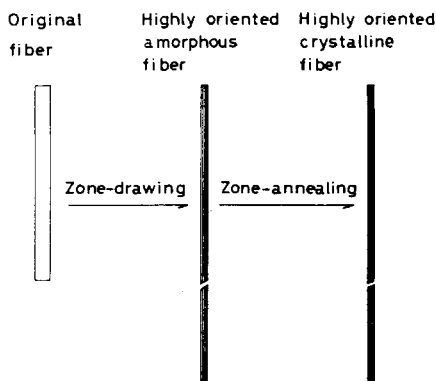


Fig. 1. Principle of the zone-annealing method.

crystals in the fiber. Since the fiber is locally heated only in the narrow heating zone, the quantity of heat required for drawing or annealing can be considerably decreased.

In spite of the low heat required, this method shows superior effects for drawing and annealing; the zone drawing transforms the fiber much easier and much faster into a homogeneous highly oriented chain structure than hot drawing or cold drawing, while the zone annealing facilitates the alignment of molecular chains and their orientation crystallization because the applied high tension acts effectively on a local area softened by heating. Furthermore, the method has the following advantages: (1) The generation of numerous nuclei can be prevented. (2) Internal distortion of crystallites is eliminated. (3) Thermal degradation of the fiber can be prevented because of the short heating time. (4) The zone-annealed fiber possesses a high dimensional stability on heating; in particular, creep does not occur at all. This represents a large difference from the structure of fibers obtained by other methods such as high-speed spinning, freeze spinning, and flash spinning.

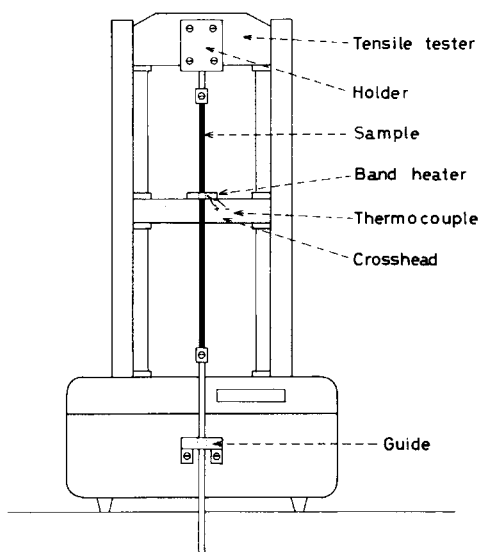


Fig. 2. Schematic representation of the apparatus used for zone drawing and zone annealing.

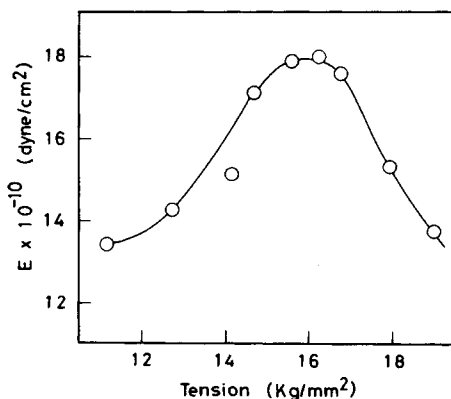


Fig. 3. Relationship between tension applied to the fiber during zone annealing and Young's modulus E of the fiber obtained.

Determination of Suitable Conditions for Zone Drawing and Zone Annealing

Although many experimental conditions can be considered in this method, the following conditions were examined in this study: temperature, the moving speed of the band heater, the tension applied on the fiber, and the number of repetitions of zone annealing.

Although the purpose of zone drawing is to obtain a fiber with as high an orientation as possible, when the zone-drawing temperature is too high, crystallization takes place; and when the tension is too large, the fiber whitens often because of local microfractures of the fiber. As a result of the examination of PET, a zone-drawing temperature of 90°C, an applied tension of 0.3 kg/mm², and a moving speed of 40 mm/min were chosen. The temperature is above the glass transition temperature (69°C) and below the cold-crystallization temperature of this polymer (120°C).

Further, the conditions for zone annealing were also examined experimentally. Figures 3 and 4 show the influence of applied tension and band heater temper-

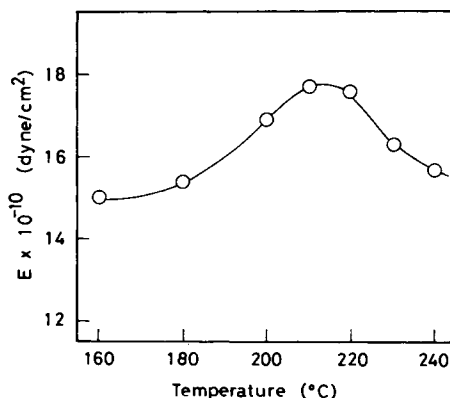


Fig. 4. Relationship between temperature of band heater during zone annealing and Young's modulus E of the fiber obtained.

TABLE I
Most Suitable Conditions for Zone Drawing and Zone Annealing

| Conditions | Zone drawing | Zone annealing |
|--|--------------|----------------|
| Temperature of heating zone, °C | 90 | 200–210 |
| Moving speed of band heater, mm/min | 40 | 10 |
| Tension applied to fiber, kg/mm ² | 0.3 | 15–16 |
| Repetition, times | — | 5 |

ature during zone annealing on Young's modulus of the obtained fibers, respectively. The maximum values of Young's modulus were obtained at 16 kg/mm² tension and in the vicinity of 210°C. The effect of repetition of the zone annealing on Young's modulus and on the strength at break of the fibers obtained was approximately constant above four times up to 10 times. Therefore, the zone-annealing procedure was repeated five times. The most suitable conditions for zone drawing and zone annealing in the range of the examination are summarized in Table I.

Mechanical Properties and Superstructure of the Fibers

Tables II and III show mechanical properties and superstructural factors of the as-spun fiber, the zone-drawn fiber, and the zone-annealed fiber, respectively. It can be seen how the properties and superstructure change in step by the two procedures. Young's modulus and the strength at break are still small in the zone-drawing stage but increase rapidly by zone annealing. The values of Young's modulus of the zone-annealed fiber, 19.4×10^{10} dyn/cm², is significantly high and corresponds to about 18% of the crystal modulus¹⁸ of this polymer along the molecular chain, 107.8×10^{10} dyn/cm².

Although the changes in the fiber structure do not perfectly follow the principle described above, it is obvious from Table III and x-ray Laue photographs (shown

TABLE II
Mechanical Properties of Original Fiber, Zone-Drawn Fiber, and Zone-Annealed Fiber

| Sample | Young's modulus, $\times 10^{-10}$ dyn/cm ² | Strength at break, kg/mm ² | Elongation at break, % |
|---------------------|---|--|---------------------------|
| Original fiber | 1.4 | — | — |
| Zone-drawn fiber | 5.6 | 14.4 | 65.2 |
| Zone-annealed fiber | 19.4 | 84.6 | 5.9 |

TABLE III
Crystallinity, Birefringence, Orientation Factors of Crystalline (f_c) and Amorphous Regions (f_a), and Relative Intensities of IR Absorption Peaks Assigned Trans and Gauche Conformations

| Sample | Crystal- linity, % | Birefrin- gence $\times 10^3$ | f_c | f_a | Trans intensity (A848 cm ⁻¹ / A795 cm ⁻¹) | Gauche intensity (A895 cm ⁻¹ / A795 cm ⁻¹) |
|---------------------|--------------------------|-------------------------------------|-------|-------|--|---|
| Original fiber | 1.8 | 0.3 | | | 0.71 | 1.52 |
| Zone-drawn fiber | 18.7 | 140.6 | 0.879 | 0.466 | 1.12 | 1.26 |
| Zone-annealed fiber | 60.0 | 247.3 | 0.986 | 0.947 | 2.78 | 0.68 |

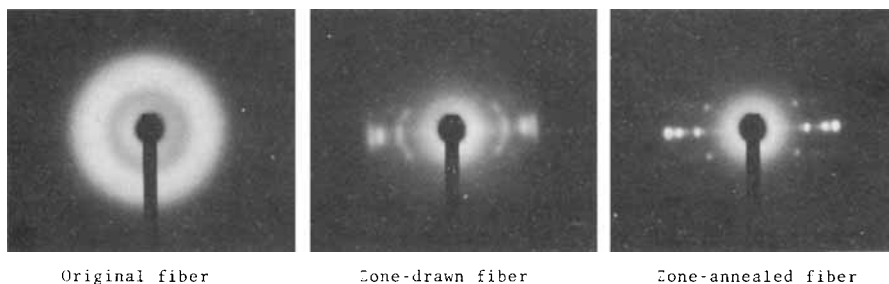


Fig. 5. X-Ray Laue photographs of the original fiber, the zone-drawn fiber, and the zone-annealed fiber.

in Fig. 5) that the zone-drawn fiber has a fairly high orientation and relatively low crystallinity, whereas the zone-annealed fiber has a very high orientation and high crystallinity. The value of birefringence of the zone-annealed fiber reached 0.247 and is higher than most¹⁹⁻²⁴ of the intrinsic birefringence values of the crystals that have been reported up to now. It can be presumed that the excellent mechanical properties of the zone-annealed fiber are based on such a high orientation, especially the orientation of amorphous chains.

Figure 6 shows the temperature dependence of the dynamic modulus E' and $\tan \delta$ for the zone-drawn and the zone-annealed fiber. In the $\tan \delta$ -temperature curves, α -dispersion peaks appeared at 110°C in the zone-drawn fiber and at 138°C in the zone-annealed fiber. The α -dispersion peak of the zone-annealed fiber is also much smaller and broader than that of the zone-drawn fiber. This fact suggests that the movement of the amorphous chains in the zone-annealed fiber is strongly prevented. This is also supported by the fact that the zone-annealed fiber has excellent dimensional stability at elevated temperatures; even when the fiber were heated to 200°C, the resulting thermal shrinkage was within

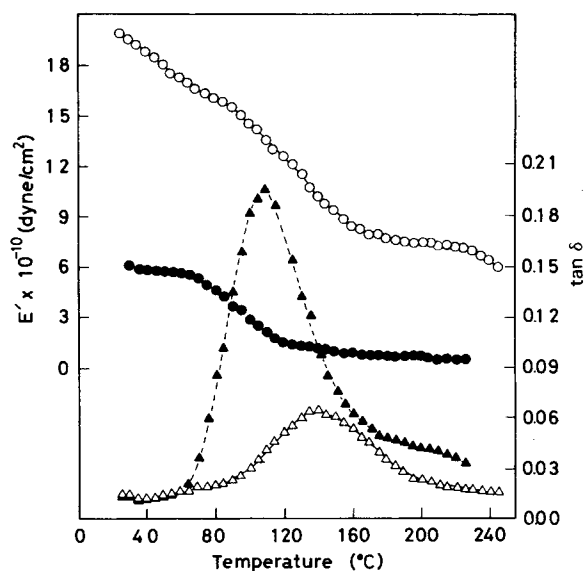


Fig. 6. Temperature dependences of dynamic modulus E' and loss tangent $\tan \delta$ for the zone-drawn fiber (\bullet and \blacktriangle) and the zone-annealed fiber (\circ and \triangle).

4% and creep could not be detected at all. It is also clear from IR data indicated in Table II that the trans conformation content of molecular segments increases and the gauche conformation type decreases in the order of the original fiber, the zone-drawn fiber, and the zone-annealed fiber. However, the IR spectrum of the zone-annealed fiber showed the presence of the 988 cm^{-1} band²⁵ assigned to a fold conformation.

From Figure 7, which shows IR spectra in the neighborhood of the fold band, it is found that the fold band seen in the undrawn and annealed fiber cannot be observed in the zone-drawn fiber, but appears as a very weak shoulderlike absorption with zone annealing. It can be presumed that the molecular end chains free from stress fold back and then crystallize as minute lamellae in the highly oriented bundle structure during zone annealing. However, the amount of the folded chain crystals seems to be very small compared with the extended chain crystals. Although it is known that two kinds of melting peaks exist in the DSC curve of PET, 258°C for the extended chain crystal and 248°C for the folded chain crystal, the temperature position of the melting peak for the zone-annealed fiber is very close to that of the former. Furthermore, small-angle x-ray scattering photographs (shown in Fig. 8) indicate that in the case of the zone-annealed fiber, the periodicity of alternating crystalline and amorphous regions along the fiber axis is fairly obscure and the estimated long period, 154 \AA , is significantly long compared with those of the fiber which was annealed under release at 200°C for 30 min after drawing up to fivefold at 90°C . The latter fiber possesses a

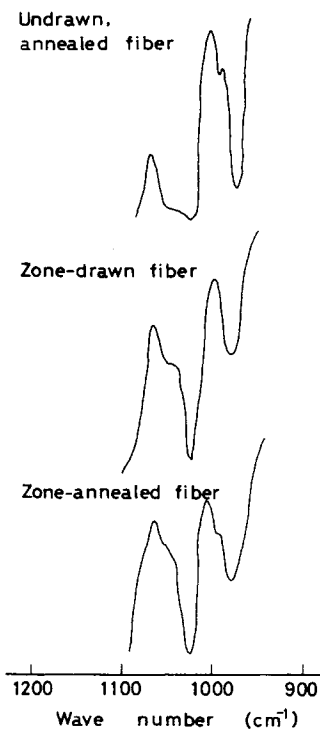


Fig. 7. IR spectra in the neighborhood of the fold band (988 cm^{-1}) of the undrawn annealed fiber, the zone-drawn fiber, and the zone-annealed fiber.

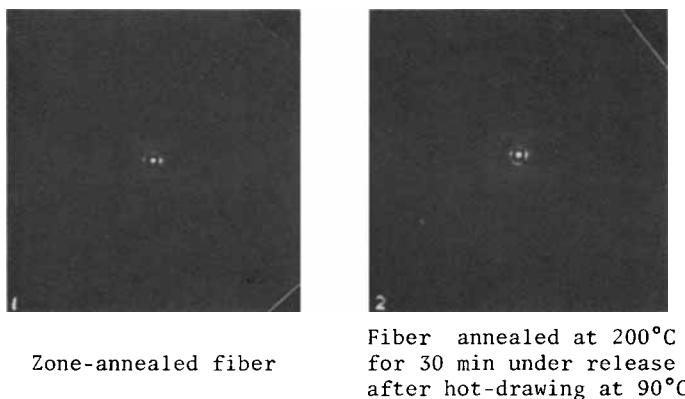


Fig. 8. Small-angle x-ray scattering photographs of the zone-annealed fiber and the fiber annealed under release at 200°C for 30 min after hot-drawing up to fivefold at 90°C.

typical lamellar structure with a long period of 118 Å. From these experimental results, the superstructure of the zone-annealed fiber was considered to be mainly a fringed micelle structure made up of highly oriented extended chain crystals and fully extended amorphous chains.

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