

Preparation of ultra-high-strength nylon-6 fibre by a multi-step zone-annealing method

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A multi-step procedure to improve the zone-annealing method was attempted to prepare a high-modulus and high-strength nylon-6 fibre. By the adoption of this procedure, the dynamic storage modulus at room temperature was markedly increased and reached 15.7×10^{10} dyne cm^{-2} which is 1.5 times that obtained by the previous zone-annealing method. Tensile properties, orientation, crystallinity and mechanical dispersion were also measured. Comparing the multi-step procedure with the previous one-step procedure, the excellent effects of the multi-step procedure on mechanical properties are discussed. Further, in order to prevent selective relaxation of amorphous molecular chains on removing the applied tension after zone-annealing, heat-setting at constant length was subsequently carried out on the as-zone-annealed fibre. The mechanical properties were further improved: for example, the dynamic storage modulus at room temperature of the resulting fibre was raised to 16.9×10^{10} dyne cm^{-2} , which was well beyond the highest modulus available in the literature, 14×10^{10} dyne cm^{-2} .

Keywords High-modulus; high-strength, nylon-6 fibre; multi-step zone-annealing; multistep zone-drawing; heat-setting

INTRODUCTION

In 1979, we proposed¹ a new method for preparation of ultra-high-strength fibres, which we called the 'zone-annealing method'. Since then this method has been applied to various polymers¹⁻¹². In spite of the simple apparatus and easy procedure, this method is able to produce a striking improvement in the mechanical properties of fibres and films. In the case of nylon-6, we could obtain a high modulus value of 10.8×10^{10} dyne cm^{-2} , which corresponded to 2.2-4.0 times that of the high tenacity fibre available commercially, as reported in the previous works^{8,9}.

Compared with other polymers, however, the extent of approach to the crystal modulus (165×10^{10} dyne cm^{-2}) is markedly low and only 6.5%, as seen in *Table 1*. This seems to be caused by insufficient unfolding of lamellae contained in the as-spun fibres as a number of spherulites. In order to increase the modulus further, it is necessary to unfold the lamellae effectively and to form a more extended chain structure.

With this intention, we have attempted a modified zone-annealing method comprised of a multi-step zone-drawing procedure. Consequently, fibres with much better mechanical properties than those of the fibre obtained in the previous studies^{8,9} could be obtained. Here we will report the results and compare the improved method with the method described in the previous papers^{8,9}.

EXPERIMENTAL

Material

The original material used in the present study is as-spun nylon-6 fibre of 0.41 mm diameter, supplied by Toray Research Center, Inc. The fibre has a birefringence of 9.5×10^{-4} and a crystallinity of 29.4%. These values differ slightly from those of the fibre used in the preceding studies^{8,9}.

Zone-drawing and zone-annealing

The apparatus is identical to that used in the preceding studies^{8,9}. However, the conditions for zone-drawing and zone-annealing differ from those described there. In

Table 1 Comparison of the maximum modulus values reached by the zone-annealing method with the crystal modulus along the molecular chains

Polymer	Maximum modulus ($\times 10^{-10}$ dyne cm^{-2})	Crystal modulus ($\times 10^{-10}$ dyne cm^{-2})	Percentage of maximum (%)
Poly(ethylene terephthalate)	21.4	107.8	19.8
Polyethylene	54	235	23
is-Polypropylene	21	42	50
Nylon-6	10.8	165	6.5

Table 2 Relationships between the repeating times, the applied tension and the birefringence in the zone-drawing stage

Repeating time	Tension applied to the fibre (kg mm ⁻²)	Birefringence (x10 ³)
1	0.90	5.3
2	3.17	46.7
3	11.80	51.3
4	18.40	53.7
5	22.95	54.9
6	30.10	54.7
7	33.60	56.7

particular, zone-drawing was repeated four times, increasing the tension applied to the fibres. This procedure is called the 'multi-step procedure'. The following abbreviations are used:

- one-step zone-drawing: 1ZD
- zone-annealing after one-step zone-drawing: 1ZD-ZA
- multi-step zone-drawing: MZD
- zone-annealing after multi-step zone-drawing: MZD-ZA

Heat-setting

A part of the zone-annealed fibres was further heat-set. Heat-setting was carried out at 190^o–200^oC for 5 min under a nitrogen atmosphere.

Measurements of mechanical properties

The tensile properties of the fibres were determined at 23^o–25^oC, RH ~65%, with a tensile tester, Tension II (Toyo-Baldwin Co., Ltd.). The length of the fibres was about 20 mm. Young's modulus, tensile strength and elongation at break were estimated from the stress-strain curves. The dynamic viscoelastic properties, E' , E'' and $\tan \delta$, were measured at 110 Hz on fibres about 20 mm long. The measurement was carried out over a temperature range from room temperature to 190^oC and at a heating rate of 1.5 C min⁻¹ in a stream of dry nitrogen.

Measurements of crystallinity and orientation

The density of the fibres (d) was measured at 25^oC by a flotation method using toluene-carbon tetrachloride mixtures. From the density obtained, the crystallinity (X_c) was calculated by the usual method using a crystal density of 1.230 and an amorphous region density of 1.084 g cm⁻².

The birefringence (Δ) was measured with a polarizing microscope equipped with a Berek compensator. In the measurements on fibres with high retardation, X - Z planes of various thicknesses cut from a single crystal of quartz were simultaneously used as additional compensators.

The orientation factor of the crystallites (f_c) was determined by the X-ray diffraction method proposed by us previously¹³ and outlined below. The bundle of fibres was placed in a fibre specimen holder mounted in the usual X-ray diffractometer, and then the X-ray diffraction intensities of two equatorial reflections, (200) and (002), were measured along the Debye ring. After corrections for polarization, absorption, background noise and incoherent scattering, the intensities obtained were further corrected by subtracting the amorphous contribution and the overlapping component arising from the adjacent crystalline reflection. The azimuthal intensity distribution

thus obtained was used to obtain the mean square sine of the angle between the reciprocal lattice vectors of each crystal plane and the fibre axis, $\langle \sin^2 \beta_{200} \rangle$ and $\langle \sin^2 \beta_{002} \rangle$. As the (200) and (002) planes do not meet at right angles, we presumed the temporary crystal plane ($h01$) to be perpendicular to the (002) and parallel to the b axis.

The mean square sine for the ($h01$) plane, $\langle \sin^2 \beta_{h01} \rangle$, can be obtained from the following equation:

$$\langle \sin^2 \beta_{h01} \rangle = \frac{\langle \sin^2 \beta_{200} \rangle - \sin^2(22.5^\circ) \langle \sin^2 \beta_{002} \rangle}{\cos^2(22.5^\circ)} \quad (1)$$

The value obtained was substituted in

$$\langle \sin^2 \alpha \rangle = \langle \sin^2 \beta_{h01} \rangle + \langle \sin^2 \beta_{002} \rangle \quad (2)$$

where α is the angle between molecular chains in the crystallites and the fibre axis. Further, by substituting $\langle \sin^2 \alpha \rangle$ in equation (3), f_c can be obtained:

$$f_c = 1 - \frac{3}{2} \langle \sin^2 \alpha \rangle \quad (3)$$

where Δ_c° and Δ_a° are the intrinsic birefringences of the crystal and amorphous phases, 0.0780 and 0.0689, respectively, which was experimentally determined by us¹⁴.

RESULTS AND DISCUSSION

Purpose and application of the multi-step zone-drawing procedure

Since nylon-6 crystallizes easily on cooling from the molten state, even as-spun fibre exhibits a fairly high crystallinity and contains a large number of spherulites, namely lamellae. The lamellae are generally difficult to unfold by subsequent procedures. However, the zone-annealing method is very effective for extension and orientation of molecular chains, because a narrow portion of the fibre is heated under high tension and the heating zone moves with a constant speed in only one direction.

One might expect that repetition of the zone-drawing would further promote the unfolding of the lamellae compared to the one-step zone-drawing used in the previous studies^{8,9}. Three kinds of techniques for the multi-step zone-drawing were considered:

- (1) The tension applied to the fibre is held constant, and the temperature of the band heater is increased gradually.
- (2) The temperature of the band heater is kept constant, and the applied tension is increased gradually.
- (3) Both the tension and temperature are increased gradually.

In the case of nylon-6, when the zone-drawing temperature is too high, crystallization takes place simultaneously. Therefore, the fibre should be zone-drawn at a low temperature close to the primary loss temperature of this polymer. For these reasons, technique (2) was adopted, and the temperature was maintained at 80^oC during zone-drawing. The applied tension, the speed of the band heater, and the number of repetitions can also be considered as important experimental conditions. Table 2 shows the relationships between the number of repetitions, the applied tension and the birefringence of the obtained fibre in zone-drawing at 80^oC and at a speed of 40 mm min⁻¹. The birefringence first increases rapidly with increased number of repetitions and tension, but

Table 3 Most suitable conditions for zone-drawing and zone-annealing

Conditions	1ZD	MZD				1ZD-ZA	MZD-ZA
		ZD-1	ZD-2	ZD-3	ZD-4		
Temperature of the heating zone ($^{\circ}\text{C}$)	80		80			180	180
Speed of the band heater (mm min^{-1})	40		40			10	300
Tension applied to the fibre (kg mm^{-2})	1.6	0.90	3.17	11.8	18.4	15.8	21.5
Repetition	1		4			6	6

1ZD: one-step zone-drawing

MZD: multi-step zone-drawing

1ZD-ZA: zone-annealing after one-step zone-drawing

MZD-ZA: zone-annealing after multi-step zone-drawing

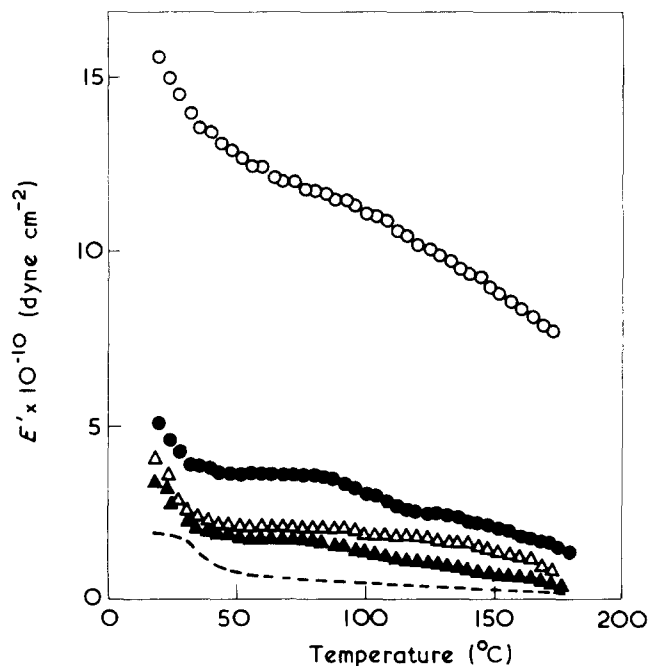


Figure 1 Temperature dependence of dynamic storage modulus E' for the original fibre (— — —), the zone-drawn fibres (\blacktriangle , ZD-2; \triangle , ZD-3; \bullet , ZD-4) and the zone-annealed fibre (\circ , MZD-ZA)

above four repetitions and 18.40 kg mm^{-2} the rate of increase becomes small. Since the purpose of zone-drawing is to obtain a fibre with a high orientation, the four-step zone-drawing under the above conditions is adequate for this purpose.

In the same manner, suitable conditions for zone-annealing were also determined after numerous preliminary experiments. The suitable conditions thus determined are summarized in Table 3.

Dynamic viscoelastic properties of the fibres in each step

Figures 1, 2 and 3 show the temperature dependences of E' , E'' and $\tan \delta$ for the fibres obtained in each step, respectively. Although the E' value increases step by step with repetitions of zone-drawing, the attainable value is still low. By zone-annealing, however, the E' value increases drastically over all the temperature range, and the value at room temperature reached $15.7 \times 10^{10} \text{ dyne cm}^{-2}$, which is 9.5% of the crystal modulus. However, a distinct loss peak is observed in the vicinity of 90°C in Figures 2 and 3. As is well known, the loss peak¹⁵ is ascribed to micro-Brownian motion of large amorphous molecular segments caused by breakdown of hydrogen

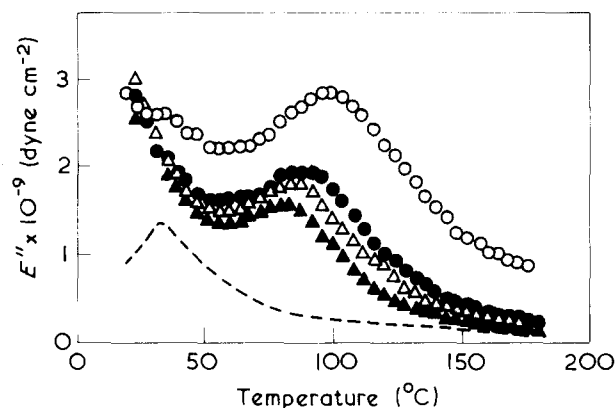


Figure 2 Temperature dependence of loss modulus E'' for the original fibre (— — —), the zone-drawn fibres (\blacktriangle , ZD-2; \triangle , ZD-3; \bullet , ZD-4) and the zone-annealed fibre (\circ , MZD-ZA)

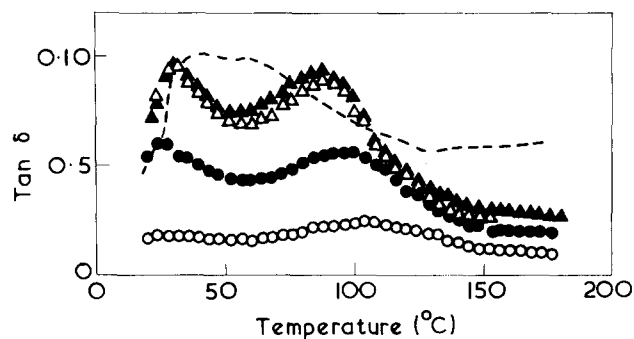


Figure 3 Temperature dependence of $\tan \delta$ for the original fibre (— — —), the zone-drawn fibre (\blacktriangle , ZD-2; \triangle , ZD-3; \bullet , ZD-4) and the zone-annealed fibre (\circ , MZD-ZA)

bonds. In Figure 2, the E'' peak increases in height and gradually shifts to higher temperatures. Since the increase in the E'' peak height implies an increase in intermolecular friction¹⁶, this fact suggests that the amorphous molecular chains are densely aggregated progressively. Also, it is clear that the $\tan \delta$ peak becomes step by step smaller and broader and shifts to higher temperatures. From such results, it is found that the movements of the amorphous molecular chains in this temperature range gradually become difficult with increasing the orientation and crystallinity.

Comparison of the multi-step procedure with the one-step procedure

By the adoption of the multi-step procedure, the applicable tension, in particular, could be greatly in-

Table 4 Comparison of mechanical properties of the fibres prepared by the multi-step and one-step procedures

Sample		Young's modulus ($\times 10^{10}$ dyne cm^{-2})	Strength at break (kg mm^{-2})	Elonga- tion at break (%)
Zone-drawn fibre	1ZD	2.28	24.3	86.8
	MZD	3.54	41.4	49.0
Zone-annealed fibre	1ZD-ZA	9.91	100.3	13.6
	MZD-ZA	11.10	96.5	10.6

Table 5 Comparison of birefringence (Δ_t), orientation factors of crystallites and amorphous chains (f_c and f_a) and crystallinity (X_c) of the fibres prepared by the multi-step and one-step procedures

Sample		Δ_t ($\times 10^3$)	f_c	f_a	X_c (%)
Zone-drawn fibre	1ZD	43.8	0.806	0.511	30.9
	MZD	51.5	0.856	0.590	41.4
Zone-annealed fibre	1ZD-ZA	60.3	0.849	0.792	48.9
	MZD-ZA	62.7	0.880	0.824	49.5

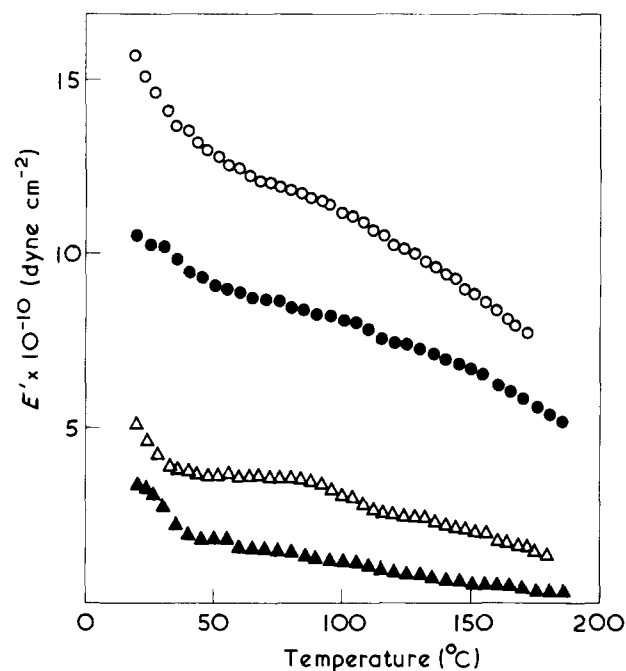


Figure 4 Comparison of dynamic storage modulus E' of the fibres prepared by the multi-step procedure and the one-step procedure: \blacktriangle , 1ZD; \triangle , MZD; \bullet , 1ZD-ZA; \circ , MZD-ZA

creased compared with the one-step procedure, that is, in zone-drawing from 1.65 to 33.6 kg mm^{-2} and in zone-annealing from 15.8 to 21.5 kg mm^{-2} . In addition, it is considered that the structure can be changed gradually and smoothly. In the multi-step procedure, the draw ratios were 2.38, 2.74, 3.75, 4.24 and 6.95 at ZD-1, 2, 3, 4 and MZD-ZA, respectively.

Therefore, the detailed comparisons of both procedures in mechanical properties and structures are of much interest in connection with the evaluation of the multi-step procedure. Table 4 shows the Young's modulus, the tensile strength and the elongation at break. Table 5 shows

comparisons of the birefringence (Δ), the orientation factors of crystallites and amorphous chains (f_c and f_a) and the crystallinity (X_c). Further, Figures 4, 5 and 6 show the temperature dependences of E' , E'' and $\tan \delta$, comparing the two procedures.

Except for the tensile strength and the E'' dispersion peak intensity, all of the mechanical properties and the structural factors of the fibres prepared by the multi-step procedure are definitely superior to those in the case of the one-step procedure. In the previous papers, we stated that the amorphous region, which has a lower modulus, has a more pronounced influence on the mechanical properties of the whole fibre than does the crystal region, by the same methods as used in the previous studies^{6,7,9,12}, the amorphous modulus (E_a) and the number and fraction of tie molecules ($(1-X_c)E_{||}^a/E_{c||}$ and β_E) were estimated. The comparisons of these values are shown in Table 6.

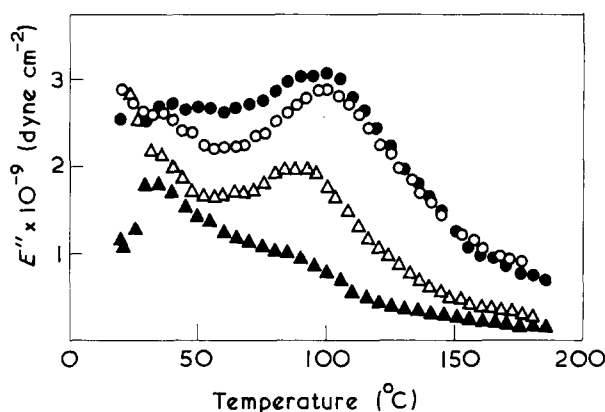


Figure 5 Comparison of loss modulus E'' of the fibres prepared by the multi-step procedure and the one-step procedure: \blacktriangle , 1ZD; \triangle , MZD; \bullet , 1ZD-ZA; \circ , MZD-ZA

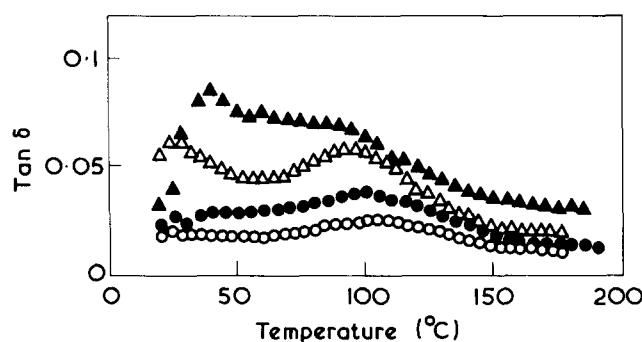


Figure 6 Comparison of $\tan \delta$ of the fibres prepared by the multi-step procedure and the one-step procedure: \blacktriangle , 1ZD; \triangle , MZD; \bullet , 1ZD-ZA; \circ , MZD-ZA

Table 6 Comparison of amorphous modulus (E_a), number and fraction of tie molecules ($(1-X_c)E_{||}^a/E_{c||}$ and β_E) of the fibres prepared by the multi-step and one-step procedures

Sample		E_a ($\times 10^{-10}$ dyne cm^{-2})	$(1-X_c)$ $E_{ }^a/E_{c }$	β_E
Zone-drawn fibre	1ZD	1.93	0.012	0.017
	MZD	2.09	0.013	0.021
Zone-annealed fibre	1ZD-ZA	5.22	0.031	0.060
	MZD-ZA	5.61	0.034	0.067

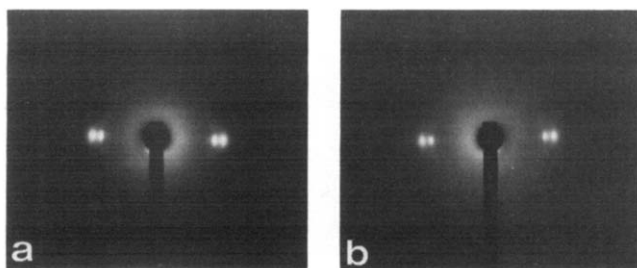


Figure 7 X-ray Laue photographs of the fibres (a) before and (b) after heat-setting

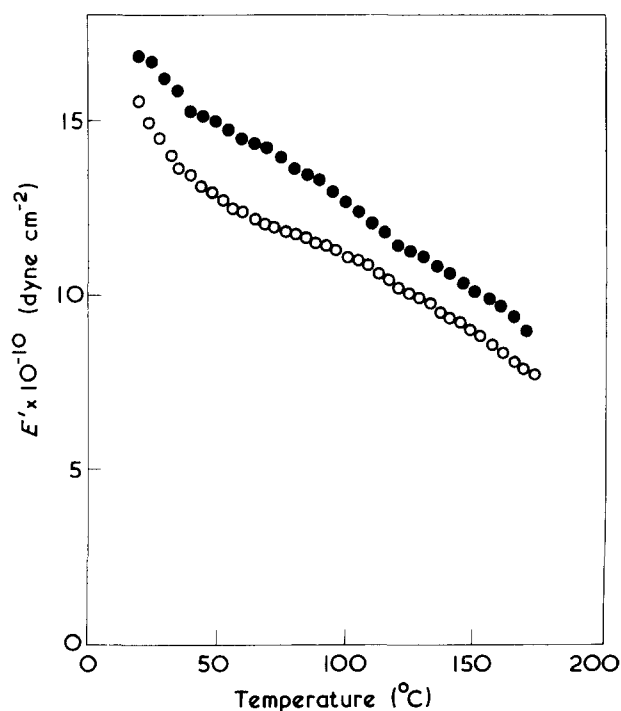


Figure 8 Comparison of dynamic storage modulus E' of the fibres before (O) and after (●) heat-setting

Based on the comparisons, it can be concluded that the multi-step procedure is very effective in increasing the taut tie molecules, which causes an increase in E_a and further results in an increase in the macro-modulus of the whole fibre.

Addition of heat-setting

In the above section, we emphasized the significance of the amorphous region in the improvement of the macroscopic mechanical properties. However, when the tension is removed after zone-annealing, an unfavourable relaxation of the amorphous molecular chains appears to take place. Then the amorphous molecular chains which were barely extended would become selectively loose and return to a slightly relaxed state. To prevent the fibre from such a relaxation, heat-setting was attempted in the following way.

After zone-annealing, the fibre was immediately fixed by a brass frame. The as-fixed fibre was heat-set at 200°C for 5 min in nitrogen and was then removed from the frame after cooling to room temperature. The fibre thus obtained has a higher birefringence of 0.066 and a much higher tensile strength of 116.9 kg mm⁻² than does the as-zone-annealed fibre.

Figure 7 shows X-ray Laue photographs of the fibres before and after heat-setting. It is clear that the X-ray reflection spots become sharp after heat-setting. Further,

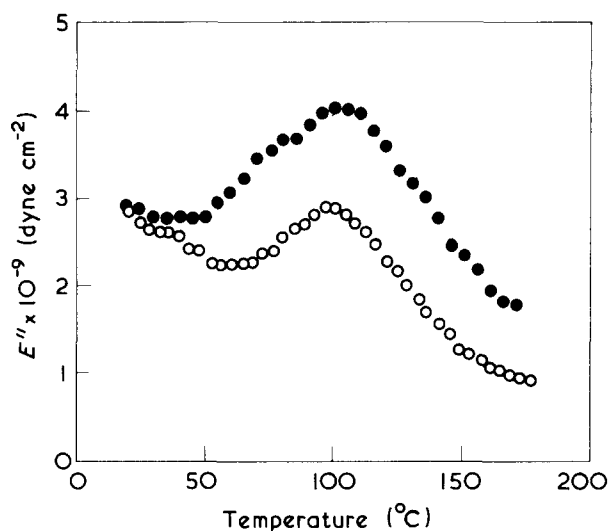


Figure 9 Comparison of loss modulus E'' of the fibres before (O) and after (●) heat-setting

Figures 8 and 9 show the temperature dependences of E' and E'' for both fibres. It is found from the figures that the movements of the amorphous molecular chains are further inhibited after heat-setting. The E' value at room temperature was increased to about 17×10^{10} dyne cm⁻² and could reach 10.2% of the crystal modulus¹⁷ along the molecular chains. This value is much higher than the E' value of nylon-6 fibre reported by Acierno *et al.*¹⁸, 14×10^{10} dyne cm⁻², which is known to be the highest value available in the literature.

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