

# ***Kinetics of Fiber Heat Treatment. I. Experimental Apparatus\****

## **INTRODUCTION**

In order to understand how processing conditions affect the morphology of polymeric fibers, it is necessary to follow the crystallization process. However, in most previous work, only the final microstructure, after long-term annealing, has been related to the processing conditions. This state of affairs is understandable, since the kinetics of fiber crystallization can be very fast, and special apparatus must be constructed if those kinetics are to be investigated.

In the kinetics of crystallization, three variables have to be taken into account: annealing time, temperature, and tension. In previous studies, however, the tension has not been controlled during the heat treatment. These studies were carried out in either of the following ways: (a) under relaxed conditions or (b) maintaining the fibers at constant length. Control of the tension gives a better characterized system. From the engineering point of view, heat treatment of fibers in an apparatus which can control the tension can also provide data for a mechanistic understanding of the crystallization process that takes place during spinning.

Studies of the kinetics of crystallization of polymeric fibers<sup>1-4</sup> have demonstrated that most of the transformation takes place at annealing times of the order of tens of milliseconds. In order to follow the course of such transformations, an experimental setup has been designed and constructed to provide annealing times within that time range, with independent control of fiber tension and temperature. Once the fibers are heat-treated, they are quenched. Microstructural changes can then be monitored at room temperature, using various characterization methods,<sup>4</sup> such as X-ray scattering, specific gravity, birefringence, and shrinkage.

## **EXPERIMENTAL**

An apparatus was designed and constructed to provide annealing times from 10 to 1000 ms, with control and measurement of: (i) temperature, (ii) time, and (iii) tension. Figure 1 depicts schematically the apparatus. (A) and (B) are two stainless steel rollers, the driver roller (A) and the winding roller (B), driven by two different motors, M1 and M2. (C) is a rubber roller set against the driver roller, both of them constituting the feed system of the apparatus. The rubber roller itself has a spring (D) with adjustable tensions. (E) is a fiber reservoir, which is attached to a vacuum cleaner. (F) is a valve to regulate the suction power. (G) is a heating head machined from a copper block. Figure 2 shows in detail the geometry of the heating head: a catenoidal shape, i.e., (i) concave outward [see cross section (b)], to spread the bundle of filaments throughout the contact surface and improving in this way the heat transfer; and (ii) concave inward [see top view (a)], to prevent the fiber from moving during the annealing process. To avoid heat losses, the heating device has a cover, shown also in Figure 2. (H) is the quenching device, made of a copper block. It has the same catenoidal shape as the heating device, and is constantly immersed in a liquid nitrogen bath. (I) is a tensiometer which reads the tension of the threadline.

The fibers are pulled out from the spool (J), and through the feeding system, in which they acquire a speed determined by the motor M1. They then enter and exit the reservoir, guided by two Teflon hooks. In the reservoir, friction from the countercurrent flow of air fixes the tension on the fiber. Next, the fibers are heat-treated in the heating device and quenched immediately. Finally, they are wound in the lower roller.

With this system it is possible to control (i) the temperature of the heating device, (ii) the tension of the threadline, regulated by the valve located in the reservoir, and (iii) the time of the heat treatment, which is determined by the speed of the winding roller (directly controlled by the lower motor M2) and the dimension  $l$  (Fig. 2) of the heating device.

The time to bring the fibers to temperature was bounded in the following way. The known geometry is approximated by one monolayer of filaments in contact with a plane of copper [Fig. 3(a)]. This geometry is functionally equivalent to that shown in Figure 3(b), where  $\bar{D}$  is

\* Work supported by the National Science Foundation under Grant No. CPE 8304058.

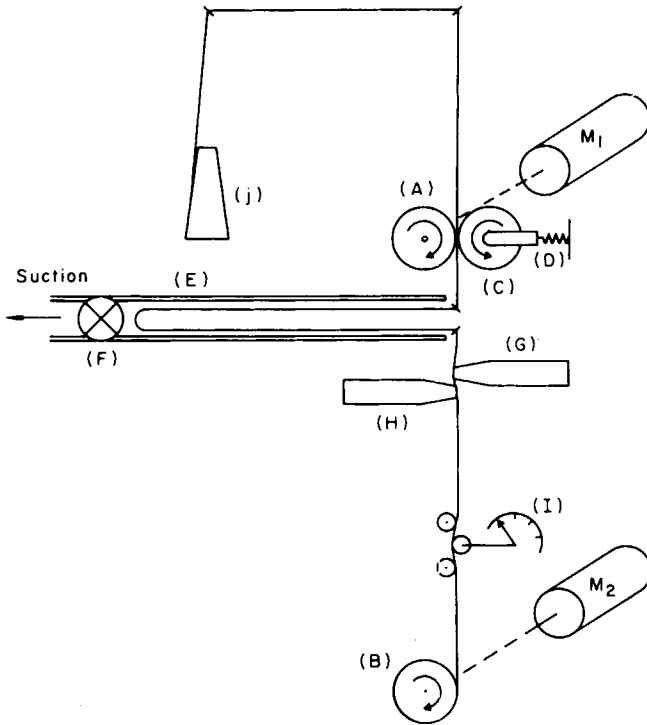
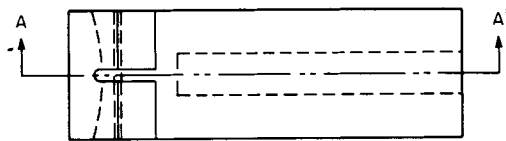
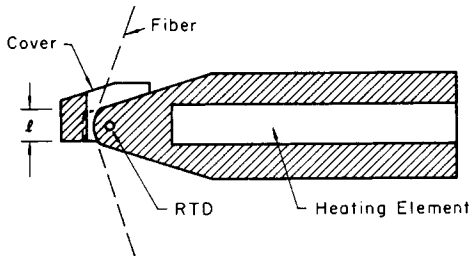


Fig. 1. Schematic of the heat-treatment apparatus.



(a) Top View



(b) Cross Section through AA'

Fig. 2. Schematic of heating head.

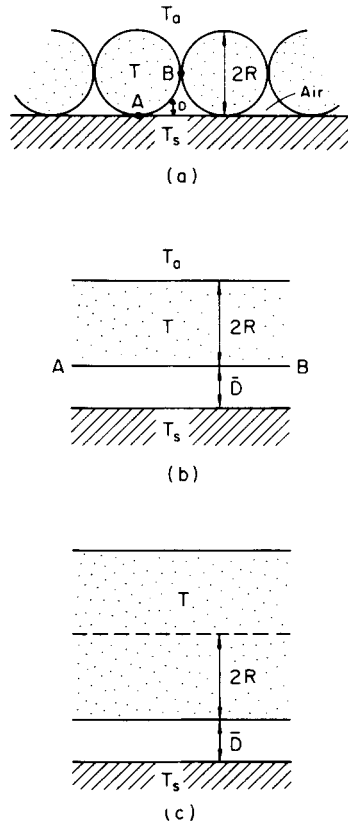


Fig. 3. Geometry for the calculation of the transient  $\tau$ .

chosen such that the integrated heat flux across  $AB$  in Figure 3(a) is identical to that across  $AB$  in Figure 3(b). Solution to this geometrical problem yields

$$\bar{D} = 0.2146R \tag{1}$$

Assuming that there are no heat losses in the  $T$ - $T_a$  interface, the geometry is analytically as shown in Figure 3(c). Now the problem reduces to the calculation of the transient heat transfer into an infinitely wide plate of thickness  $4R$ . This is a well-known problem, whose solutions are tabulated.<sup>5</sup> The reduced variables of this problem are (1) the Biot number and (2) the reduced temperature,  $\theta = (T_s - T)/(T_s - T_a)$ . The Biot number is given by

$$\frac{1}{m} = \frac{h \cdot 2R}{k_p}$$

where  $h$  is the heat transfer coefficient between heating surface and polymer and  $k_p$  is the thermal conductivity of the polymer. The heat transfer coefficient  $h$  is given by

$$h = k_{\text{air}}/\bar{D} \tag{2}$$

where  $k_{\text{air}}$  is the thermal conductivity of air. Thus the inverse of the Biot number is

$$m = \frac{k_p \cdot 0.2146R}{k_{\text{air}} \cdot 2R} \quad (3)$$

Using values appropriate to our system ( $k_p = 0.16$  w/mK,  $k_{\text{air}} = 0.04$  w/mK,  $R = 10$   $\mu\text{m}$ ), one finds  $m = 0.43$ . To find the time  $\tau$  to attain 90% of the temperature increase— $\theta = 0.1$ —one finds the tabulated value (5) of the Fourier number

$$F_0 = \frac{\alpha_p \tau_1}{(2R)^2} \quad (4)$$

consistent with  $m = 0.43$  and  $\theta = 0.1$ . Using  $0.6 \times 10^{-3}$   $\text{cm}^2/\text{s}$  for the thermal diffusivity  $\alpha_p$  of the polymer, one obtains for the transient time  $\tau_1 = 13$  ms.

The above case, a monolayer of filaments, with each filament in contact at only one point with the surface, can be taken as the worst case. In the real case, the contact is more distributed, since heat and stress flatten the filaments against the substrate.  $\tau_1$  is thus an upper limit. To find a lower bound, we consider perfect contact—i.e.,  $m = 0$  and  $F_0 = 1$ . For this case, the transient time,  $\tau_2$ , is 6 ms. The real transient lies between these bounds ( $\tau_1$  and  $\tau_2$ ) and should be near 10 ms.

### EXAMPLE HEAT TREATMENT

Figure 4 shows, for purposes of illustration, shrinkage data vs. annealing time of as-spun PET fibers, heat-treated at 120°C and 2 g of tension. The fibers were marked before the heat treatment, and measurements of those marks were taken after annealing. These data provide the shrinkage  $S$ , defined as

$$S = \frac{L_0 - L_f}{L_0} \times 100$$

where  $L_0$  and  $L_f$  are the initial and final lengths. In this figure, data from two different runs are given. One sees that the reproducibility of the data is excellent.

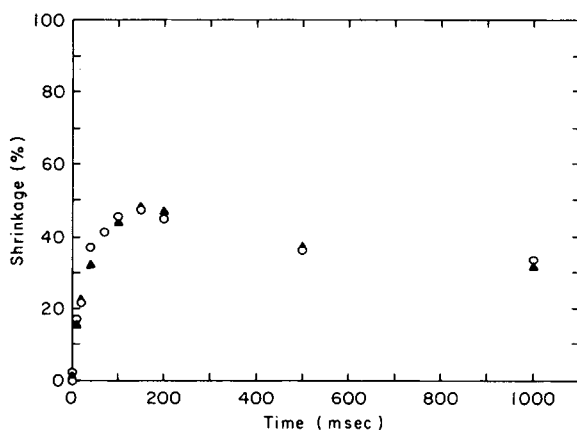


Fig. 4. Shrinkage of PET fibers heat-treated at 120°C and 2 g in tension vs. annealing time: (○) first run; (▲) second run.

We are indebted to Messrs. Jack Hollobaugh and Arthur Baeckel for the construction of the apparatus.

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Received July 19, 1984

Accepted October 2, 1984