

The Collapse Process in Acrylic Fibers

INTRODUCTION

Acrylic fibers produced by wet spinning have a fibrillar, porous structure consisting of a network of rods or fibrils.¹ The network is oriented by drawing, and the pores become elongated in the direction of stretch. The drawing step is usually conducted in boiling water, and so the drawn fibers are wet. This water is removed in the drying operation by heating the drawn fibers. However, major structural changes occur on heating since the porous nature of the fibers is eliminated and the fibrillar structure is no longer evident. The drying is accompanied by a radial contraction of the fibers, and so this step is alternatively known as the collapse stage.

The wet spinning process has been extensively studied.¹⁻⁶ There has been rather less work on the drawing step, and here the studies of Knudsen and Fitzgerald⁷ may be cited as a natural extension of earlier work on cellulose.⁸ The processes occurring during collapse have, as yet, received little attention.

The purpose of this work is to give the results of a study on drying and collapse. Emphasis is placed on the fundamental aspects rather than on details of processing. Since it has been established that orientation is not a prerequisite for collapse⁹ the study is confined to collapse of unoriented fibers.

EXPERIMENTAL

The polymer used was a copolymer of 93% acrylonitrile and 7% vinyl acetate. The polymer was dissolved in dimethylacetamide (DMAc) to give a solution containing 27.5% polymer by weight. The solution was pumped through a 100-hole spinnerette immersed in a spin bath containing a solution of 55% DMAc and 45% water by weight. The temperature of the spin bath was 40°C. The aqueous DMAc solution served as a coagulant for the filaments emerging from the spinnerette. The coagulated fibers were allowed to sink to the bottom of the spin bath. After collection of a sufficient quantity of fiber, the fibers were removed from the bath, washed in water, and freeze dried using liquid nitrogen.^{1,5} This procedure preserved the fibrillar nature of the samples. Fibers produced in this manner correspond to the "model fibers" used by Hermans¹⁰ in the study of cellulose and possess several advantages over fibers produced in the normal manner. Model fibers have a circular section, possess little or no spin orientation,⁴ and have a less pronounced skin.

Fibers were studied under a variety of heating conditions and under various restraints, e.g., free or at constant length. The diameter of the fibers was measured as a function of temperature using a microscope and, in some cases, at room temperature after heat treatment. Sonic velocity measurements were made at room temperature with a KLH pulse propagation meter at a frequency of 5000 c/s under a tension of 0.05 g/d. Load-extension curves were obtained at room temperature on an Instron testing machine at an extension rate of 100%/min.

The glass transition temperature was estimated from creep rate measurements; the creep rate of a sample sharply increases in the glass transition region.

RESULTS

Figure 1 shows the load-extension curve for a model fiber. After the yield point, the load is constant with increasing elongation until fracture at an elongation of 55%.

The creep rate measurements show that the glass transition temperature for the model fibers is near 100°C at 0% relative humidity. At 100% relative humidity, the glass transition temperature is near 70°C.

There are several parameters which could affect collapse, including temperature and time at temperature, method of heating, and restraining sample, water content of sample, and the condition of the sample, e.g., orientation of sample. Experiments regarding

the effect on collapse of these conditions show that the important parameter is the temperature at which the fiber is heated; this temperature must be in the neighborhood of the glass transition temperature for collapse to occur. The influence of water is to cause collapse at a lower temperature. The influence of time at temperature is seen above the glass transition temperature where time and temperature become interchangeable, i.e., the same change occurs in a short time at a particular temperature or in a longer time at a lower temperature.

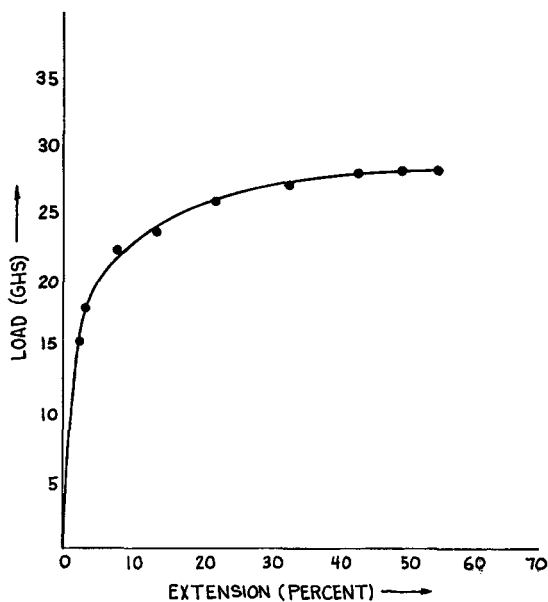


Fig. 1. Load-extension curve for a model fiber.

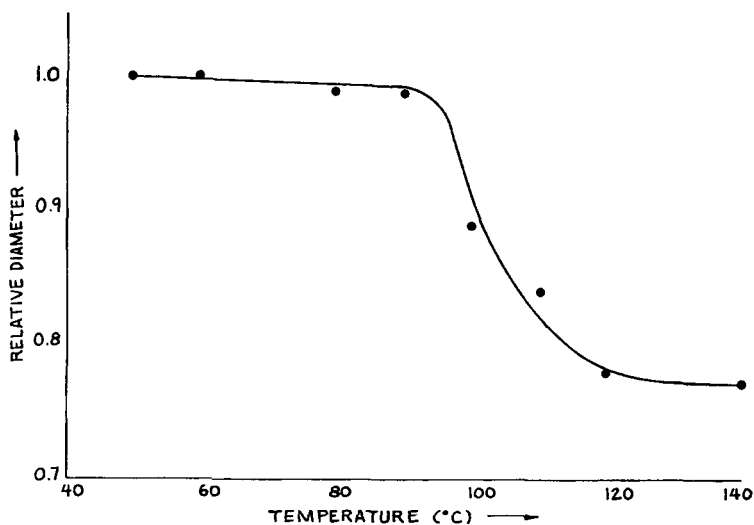


Fig. 2. Change of diameter with temperature for a model fiber heated in air under relaxed conditions.

Several changes in the fiber properties occur on collapse. Figure 2 shows the change of diameter with temperature for a fiber heated in air under relaxed conditions. The diameter decreases sharply at a temperature of 90°C, and collapse is essentially complete at a temperature of 130°C. The diameter change is accompanied by a shrinkage of the fiber, as shown in Figure 3. The shrinkage is also complete at a temperature of 130°C. The decrease in porosity which accompanies collapse is revealed in the increase of the sonic modulus of the fiber. Figure 4 shows the sonic modulus, measured at room temperature, as a function of temperature of heat treatment. The sonic modulus has an abrupt increase in the temperature region in which collapse occurs.

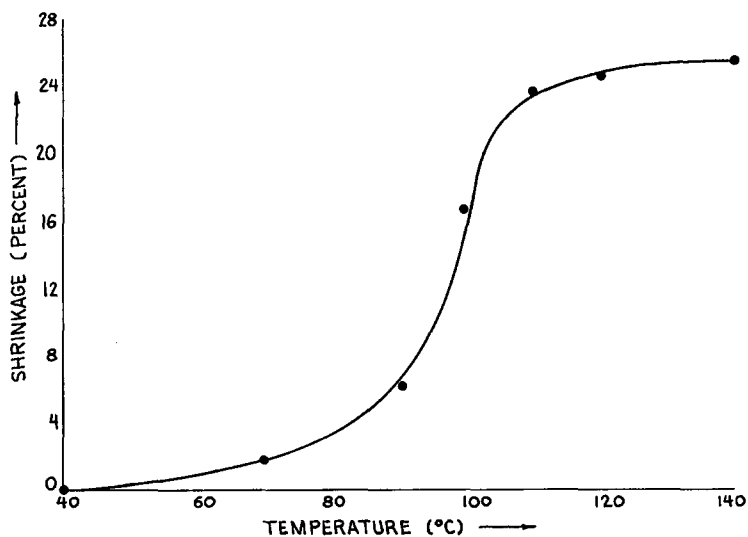


Fig. 3. Shrinkage as a function of temperature for a model fiber.

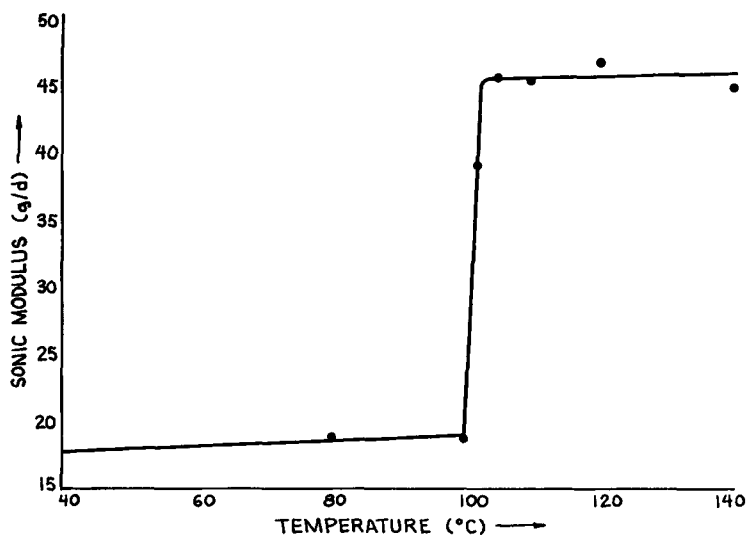


Fig. 4. Sonic modulus of a model fiber as a function of temperature of heat treatment.

DISCUSSION

It is necessary to discuss the present concept of the structure of acrylics before proceeding to a description of the mechanism of collapse. A recent survey on the subject has been given by Bell and Dumbleton.¹¹ In brief, the polyacrylonitrile molecule is thought to adopt a helical conformation. The fibrils consist of arrays of helical molecules which pack with lateral but not longitudinal order. The molecules may be straightened or partially straightened by application of a tensile stress. The drawing process consists primarily of orientation of the fibrils, possibly followed by a stretching of the helices. Slip will also occur above the glass transition temperature.

It is proposed that the helices are already extended in the model fibers. This proposal is supported by the shape of the load-extension curve which may be explained as the consequence of orienting the fibrillar network. There is no straightening of the molecule, which would appear as an increase in load with increase in extension, because the molecules are already extended from the coagulation process. A similar situation occurs in poly(vinylidene fluoride).¹²

The dependence of the collapse process on the glass transition temperature implies that collapse depends on the mobility of chain segments. The influence of water causes collapse at a lower temperature because of the increased mobility of the chains. Bearing in mind the discussion on structure, it is suggested that the process occurring in collapse is the retraction of fibrils caused by the molecules returning to a helical conformation. This process will cause both a decrease in the diameter of the fiber and a decrease in length (shrinkage). Suppose that the equilibrium length of a fibril is L_0 and the stretched length is L . The average projected length before collapse is

$$L \int_0^{\pi/2} \sin^2 \theta d\theta \text{ i.e., } \frac{\pi}{4} L$$

in the direction perpendicular to the fiber axis, where θ is the angle between a fibril and the fiber axis. After collapse, this length is $(\pi/4)L_0$. The ratio of diameters before and after collapse is $L:L_0$. If the difference between L and L_0 is due to the stretching of helices, then, for reasonable helix angles, the maximum value of L is about $1.4 L_0$. Thus, the maximum ratio of diameters is 1.4:1. Figure 2 shows that the measured ratio is 1.3:1. The shrinkage accompanying collapse is given by $[(L - L_0)/L] \times 100\%$, i.e., a maximum of 29% shrinkage. The shrinkage given in Figure 3 is 26%, which is within the limit and is in reasonable agreement with the shrinkage of 23% calculated on the basis of the measured diameter ratio.

The mechanism just proposed is responsible for the major part of the diameter change seen during collapse and is the initial mechanism by which the diameter decreases. However, this mechanism cannot be the only one operative because there would still be voids left in the structure after the fibril relaxation was complete. The second mechanism of collapse is less accessible to observation since it is not associated with a large diameter change. On the other hand, this mechanism is structurally the more important since it involves a consolidation of the structure which can only be achieved by a breaking and reforming of junctions at the fibril ends, so that on completion there is no visible evidence of the fibrillar nature of the material. It is also possible that actual bonds are formed between the fibrils themselves, i.e., along the length of neighboring fibrils and not just at the ends. The consolidation stage of collapse will determine the stability of the structure to reswelling.

CONCLUSION

The evidence suggests that a two-stage process is responsible for the collapse of acrylic fibers. The first step consists of a retraction of stretched molecules to a helical conformation, while the second step consists of a restructuring of the network to eliminate the pores. In the second step network junctions form, and so the collapsed structure is

stabilized against reswelling. It may be noted that similar mechanisms are probably operative in the collapse of cellulose.^{13,14}

References

1. J. P. Craig, J. P. Knudsen, and V. F. Holland, *Text. Res. J.*, **32**, 435 (1962).
2. D. R. Paul, *J. Appl. Polym. Sci.*, **12**, 383 (1968).
3. D. R. Paul, *J. Appl. Polym. Sci.*, **12**, 2273 (1968).
4. D. R. Paul, *J. Appl. Polym. Sci.*, **13**, 817 (1969).
5. J. P. Knudsen, *Text. Res. J.*, **33**, 13 (1963).
6. W. E. Fitzgerald and J. P. Craig, *Appl. Polymer Symposia*, **6**, 67 (1967).
7. J. P. Knudsen and W. E. Fitzgerald, paper presented at the Gordon Research Conference on Textiles, New London, New Hampshire, 1965.
8. P. H. Hermans, *Physics and Chemistry of Cellulose Fibers*, Elsevier, Amsterdam, 1949, pp. 397-425.
9. J. H. Dumbleton, unpublished work.
10. P. H. Hermans, *Physics and Chemistry of Cellulose Fibers*, Elsevier, Amsterdam, 1949, p. 385.
11. J. P. Bell and J. H. Dumbleton, in preparation.
12. R. P. Teulings, J. H. Dumbleton, and R. L. Miller, *Polymer Letters*, **6**, 441 (1968).
13. P. H. Hermans, *Physics and Chemistry of Cellulose Fibers*, Elsevier, Amsterdam, 1949, p. 380.
14. V. C. Haskell, *J. Polym. Sci. C*, **28**, 289 (1969).

J. H. DUMBLETON

Materials Science Dept.,
University of Cincinnati, Ohio 45221

J. P. BELL

Department of Chemical Engineering
U-139
University of Connecticut
Storrs, Connecticut 06268

Received June 15, 1970