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Tensile Response of Polyacrylonitrile Fibers During Air Heating

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Synopsis

Axial stresses generated by polyacrylonitrile filaments heated in air at constant length and length changes of filaments heated at constant load were measured. Fibers subjected to loads less than about 0.1 gpd shrank in the temperature range from about 40°C to 160°C. At about 160°C they began to stretch. Fibers that stretched out again to about their original lengths stiffened temporarily before undergoing a further elongation. At a temperature where the oxidation reaction begins to proceed with appreciable rate, elongation was retarded and finally reversed. Shrinkage was recorded during isothermal heating at 270°C, and a final length was approached when the oxygen content approached about 10 wt-%. The tension generated when the fibers were restrained from shrinking increased as temperature increased to 160°C but dropped in the temperature range of 160° to 250°C. Tension again built up during isothermal oxidation at 270°C. In the case of one of the samples, the tension generated below 160°C exceeded the ultimate tensile strength of the fibers above 200°C. This condition leads to tensile failures when the filaments are heated in a steep thermal gradient. The tensile behavior of the filaments is discussed in terms of the helical molecular model.

INTRODUCTION

The work of Andrews and co-workers on the rheo-optical properties of cast acrylic films,[1–3] of Rosenbaum[4] on the mechanisms of tensile response of drawn acrylic fibers, and of Kobayashi et al.[5] on thermal contraction of polyacrylonitrile fibers are examples of studies which indicate the complexity of phenomena related to structural changes that occur when acrylics are heated. Bell and Dumbleton[6] have recently reviewed much of the literature relating to structure and structural changes in acrylics and find this previous work to be consistent with the conclusion that the PAN molecules occur in the form of an irregular helix, with the degree of irregularity along the chain unspecified. They propose a model in which the molecules are in helical conformation in the relaxed state and can extend during deformation. These molecules are arranged in fibrils which in turn form a three-dimensional network. Stages in the processing of acrylic filaments tend to align the fibrils and extend the helices. They found the mechanisms of deformation of dried fibers to be in agreement with the observations of Rosenbaum,[4] who has explained stress–strain behavior in terms of an initial glassy deformation, followed by a large extension below the glass transition temperature attributed to straightening of the twisted molecules, and finally permanent

relative displacements of fiber elements (plastic flow) above the glass transition.

During the course of recent studies concerned with the oxidation and carbonization of acrylic fibers, it was observed that some types of fibers could be oxidized at constant length while subjected to a regime that included their passage through a steep thermal gradient, whereas others would break in the gradient. The failure of the latter fibers was clearly related to tensile forces generated in the fibers during the heat treatment, but no quantitative data relating to this behavior were found in the literature. Consequently, a series of experiments was undertaken to help characterize this behavior. This included measurements of axial stress generated by the fibers when heated at constant length and length changes of fibers heated at constant load. The results of these measurements could be interpreted in terms of the helical, or springlike, molecular model.

EXPERIMENTAL

Heating the filament tows was carried out in a 5-ft vertical muffle. Shop air was passed through a preheater and thence into the bottom of the muffle. Independently controlled heater tapes on the outside of the muffle compensated for heat losses along its length. Temperature profiles at different times after power was applied are shown in Figure 1. A shallow gradient existed during heat-up, but after about 20 min the temperature was uniform over the entire length of the muffle. In order that the tows not pass through the steep gradients at the ends of the muffle, 4-ft lengths of tow were tied to special bushings having wire leaders that led outside the muffle.

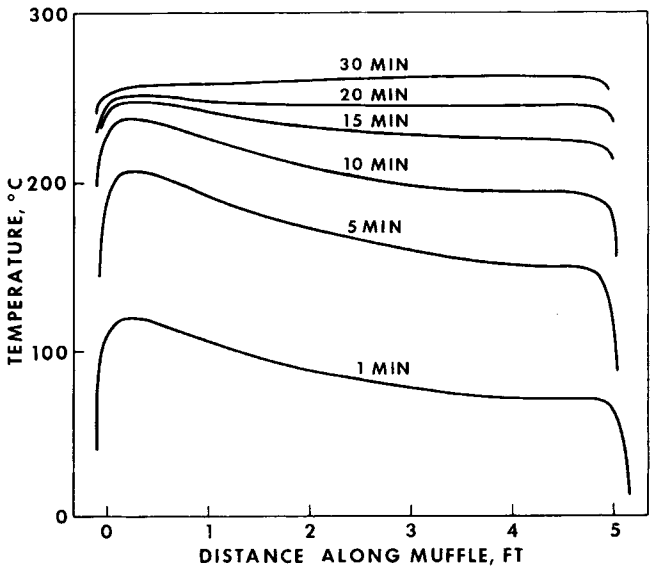

Fig. 1. Temperature profiles in heating muffle after applying power.

Thus, the entire length of the tows could be positioned in the uniform temperature zone. In order to measure length changes during air heating, the upper wire leader was clamped to a rigid support, and various weights were hung from the lower leader and the position of the weight read from an adjacent meter stick. In order to measure the stresses generated in the tow during heating at constant length, the lower leader was rigidly clamped and the upper leader was connected to a calibrated ATC load cell the output of which was recorded on an x-y plotter.

RESULTS

Typical results of the elongation experiments are shown in Figure 2, along with some data replotted from Rosenbaum's[4] Figure 4. Sample A was an experimental wet-spun PAN homopolymer which exhibited tensile failures when heated in a thermal gradient, and sample B was a commercial dry-spun homopolymer which survived similar treatment. The data indicate that the samples had some common characteristics. Essentially elastic behavior under low loads was exhibited at temperatures up to about 40°C (region I of Fig. 2). Above this temperature, larger deformations took place: shrinkage in the case of low loads, stretching in the case of high loads exemplified by Rosenbaum's data. In the case of high loads, while only elongation is observed, inflections in the curves appear to mimic the gross inflections observed at low loads. However, the precision of replotting Rosenbaum's data is perhaps not sufficient to permit much significance to be attached to this. An interesting transitional behavior in this temperature regime was observed for sample B under a load of 0.13 gpd, where a slight initial elongation was later reversed and followed by an equally slight shrinkage. At temperatures in the neighborhood of 160°C, the mode of deformation changed and samples under low load that exhibited shrinkage at lower temperatures began to stretch (region IIIa). An interesting phenomenon was observed here: samples that had previously exhibited shrinkage and that later stretched out to at least their original lengths exhibited a transitory stiffening at about their original lengths before stretching at an accelerated rate (region IIIb). Stiffening was not observed in the case of sample A under a load of 0.09 gpd; rather, after reaching the original length, failure occurred rapidly at a small total strain. Sample B loaded to 0.13 gpd stretched to the limit possible in the apparatus, so it is not known whether it would have failed under this load or would have recovered. If samples did not fail in region IIIb, elongation slowed, and at a temperature in the neighborhood of 260°C elongation ceased and shrinkage began again (region IV) and proceeded until some constant length was approached. The time scale of this complex rheological behavior is shown in Figure 3, where the dimensional changes exhibited by sample A are plotted against time.

The curves of tension developed in the tows during heating at constant length are shown in Figure 4 and are seen to parallel the behavior of the con-

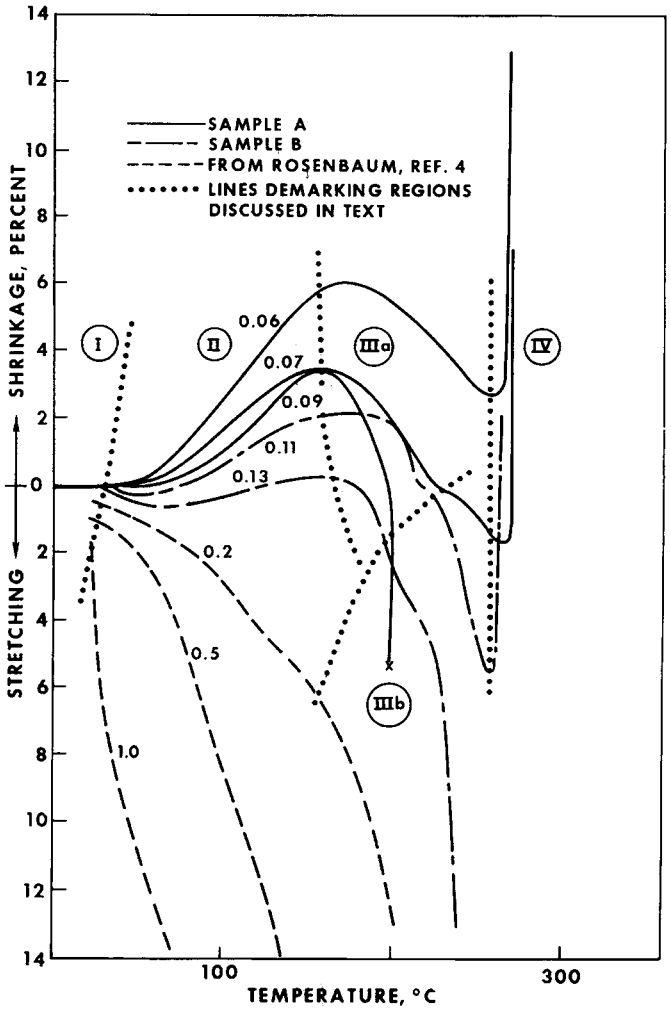

Fig. 2. Dimensional changes of acrylic filaments under load during air heating as functions of temperature. The parameter labeling each curve is the initial load placed on the sample in grams per denier (gpd).

stant load curves. During heat-up to about 150°C, considerable tension was generated within the filaments. Filaments which are subjected to lesser loads than this tension shrink in this region, whereas the data of Rosenbaum indicate that filaments subjected to greater loads stretch. Note that the transitional behavior shown for sample B in Figure 2 occurs when the load is very nearly equal to the tension generated by this sample at constant length, namely, 0.135 gpd. For temperatures between about 150° and 250°C, the tension fell rapidly and filaments under even small loads stretched. Above 250°C, tension again built, resulting in the shrinkage observed in the constant load experiments.

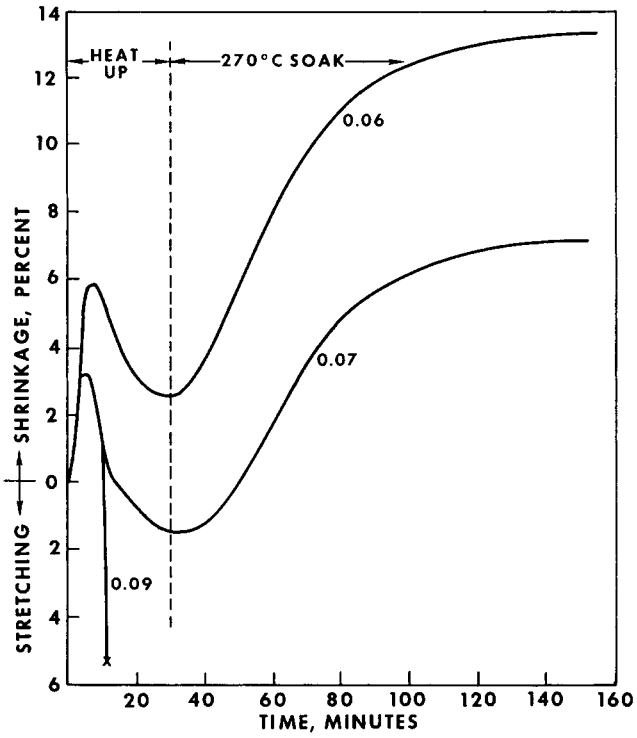

Fig. 3. Dimensional changes of acrylic filaments (sample A) under load during air heating as functions of time.

DISCUSSION OF RESULTS

The tensions generated at constant length and the elongations exhibited at constant load when the polyacrylonitrile tows were heated in air can be related to structural models proposed by previous authors. Rosenbaum describes the major extension below the glass transition temperature as due to the straightening of twisted molecules against the intramolecular repulsion of adjacent dipoles. In the present work, one may likewise attribute the major changes in filament length in region II of Figure 2 to the natural tendency of the molecules to assume a twisted or helical configuration. Under small loads (i.e., the axial stress on the molecules is less than the stress required to extend the molecules during the stretching stage of fabrication, see ref. 6), the intramolecular repulsion causes a further twisting of the elongated molecules, which probably accounts for the tension developed in the constant length experiments and the shrinkage observed in the constant load experiments.

In the view of Rosenbaum, the major part of the deformation above the glass transition temperature occurs by plastic flow, although the main

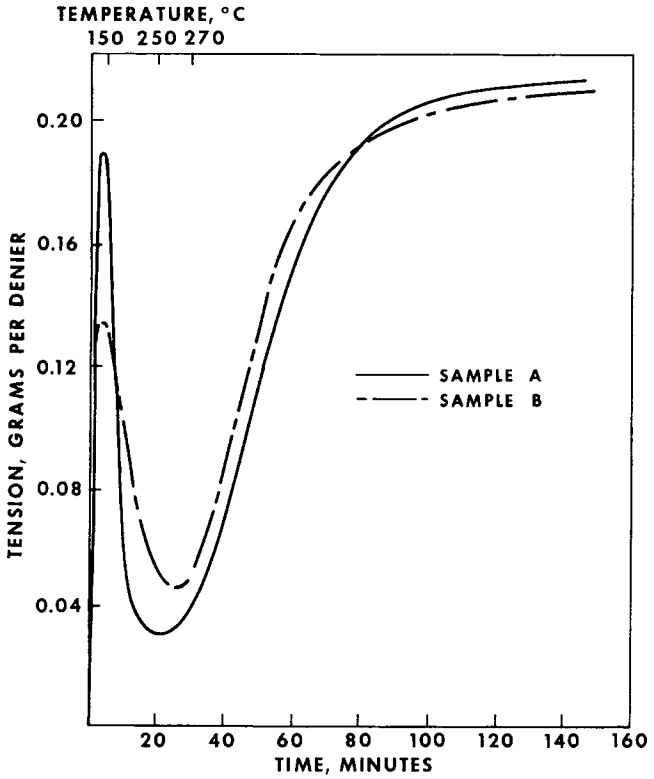

Fig. 4. Tensions generated by acrylic filaments restrained to constant length during air heating.

mechanism for extension below the glass transition temperature (namely, untwisting of coiled molecules) also provides the initial response above T_g. The deformation observed in region IIIa of Figure 2 can be interpreted in terms of a lowering of the dipole interactions which cause twisting of the chains. As this interaction weakens, the chains which coiled back under low loads below the glass transition now begin to stretch out again until the molecular configuration approximates that of the original filaments. At that point, the fibers stiffen because a substantial portion of the chains is again fully extended. Further deformation (region IIIb) then occurs by irreversible flow as indicated by Rosenbaum.

In region IV, it may be assumed that structural changes due in all likelihood to a number of competing reactions [7] arrest further plastic flow and cause the fibers to contract. Although the details of the processes which cause contraction are not known, undoubtedly the formation of strong bonds and the fact that a weight loss occurs during the oxidation are contributing causes.* Although this final shrinkage has been observed to begin

* *Note added in proof:* D. J. Müller et al.,[9] discuss the shrinkage that occurs during oxidation in terms of the cyclization of PAN to imperfect ladder networks.

at a temperature around 260°C under the given experimental conditions, it may be assumed that shrinkage would occur at lower temperatures, given sufficient time.

Figures 3 and 4 indicate that shrinkage under load and tension generated at constant length reach limiting values as the reactions proceed. In another communication,[8] the change in oxygen content with time during isothermal oxidation of similar PAN fibers was shown. It can be seen that the tension- and length-versus-time curves in region IV parallel the oxygen content curves. When the filaments have absorbed about 10 wt-% oxygen, they have become essentially flame proof, and they also cease to shrink further.

From the data presented, it is clear why sample A broke when oxidized in a regime involving passage through a thermal gradient, whereas sample B did not. Filaments of A in region III have an ultimate tensile strength or tenacity somewhere between 0.07 and 0.09 gpd and exhibit a relatively low strain at failure of about 5%, whereas the tensions generated in this sample in regions II and IV are approximately 0.2 gpd. A fiber passing through a thermal gradient such as that existing at the ends of the muffle (Fig. 1) will have different portions of its length exposed to the different regions simultaneously. Region III will be just inside the muffle, and this is where failure was observed to occur shortly after the start of heat-up. On the other hand, fibers that exhibit properties similar to these of sample B have sufficient tensile strength in region III to withstand tensile forces generated in region II and sufficient strain capability to relieve the stresses generated in region IV, and consequently do not fail.

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