

Volume Contraction and Its Significance in Structural Formation During the Thermal Stabilization of Acrylic Fibers

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Synopsis

The length changes of acrylic fibers during isothermal treatment at temperatures from 208°C to 270°C were measured under constant tensile stresses. In order to elucidate the relation between the length and structural changes during heat treatment, the measurements of density, the elemental composition, and the aromatization index determined from X-ray diffraction were made for the fibers heat-treated at 252°C for various periods of time. It is shown that a contraction in length which accompanied a volume contraction occurred during extended heat treatment, even when the fibers were subjected to high tensile stresses. The volume contraction is attributed to the fact that planar cyclized polymer segments, formed by additional polymerization of the nitrile side groups, are built up and construct a stacking which is denser than the original fiber structure. The orientation of the stacking of the cyclized segments was measured for the fibers heat-treated in the fixed state giving a high orientation, which is comparable to that of the fibers heat-treated under a high tensile stress giving an extension to the fibers in the initial periods of heat treatment. These results were explained by considering the interaction of external constraint and volume contraction which occurs during heat treatment.

INTRODUCTION

In processing acrylic fibers to produce carbon fibers, a low temperature treatment in air is normally required prior to carbonization. This low temperature treatment leads to the formation of a cyclized structure due to additional polymerization of the nitrile side groups.¹ The cyclized structure is stable towards heat and is converted to turbostratic carbon with a minimum loss of weight.² The low temperature treatment is often referred as stabilization. During stabilization acrylic fibers contract or extend longitudinally in response to loads applied to the fibers. Watt and Johnson³ have found a relation between the length change during stabilization and the tensile modulus of resulting carbon fibers; acrylic fibers which have extended gave a relatively higher modulus while those which have contracted gave a low modulus. Controlling the length change during stabilization is technologically important in optimizing the mechanical properties of carbon fibers. The length contraction which is developed during stabilization under small applied stresses is caused chemically,^{4,5} and can be used as a measure for evaluating the optimum time of stabilization.^{6,7}

Fitzer and Muller⁴ have explained the length contraction in terms of the intra- and intermolecular cyclization reactions between the nitrile side groups. In their argument the intra- and intermolecular cyclization proceed at different ratios, and, consequently, polymers with angled partial ladder structures are formed.

The linear length of sequences becomes shorter by forming angled ladder structures than that of the original sequences. This causes the length contraction of fibers.

Acrylic fibers exhibit a considerable increase in density during stabilization.^{8,9} There is a possibility, therefore, that a contraction in volume could take place during the treatment, though the density increase does not necessarily indicate the existence of volume contraction since the fibers undergo a complex change in mass due to dehydrogenation and oxygen incorporation.^{9,10}

In this work a number of measurements were made to clarify the fact that acrylic fibers develop during stabilization a volume contraction simultaneously with the length contraction. The effect of the heat treatment under conditions constraining the length contraction on the orientation of structure of the treated fibers was investigated. The volume contraction is explained in terms of the formation of the stacking of the cyclized segments.

EXPERIMENTAL

Material. Acrylonitrile copolymer fibers containing methylacrylate as the major comonomer were used in this study. The acrylic fibers were in the form of continuous filament yarn of 161 tex, comprised of 1000 filaments. The acrylic fibers had the following elemental analysis: C, 67.2%; N, 4.9%; H, 5.9%; O, 2.0%.

Length Changes. The length changes of the acrylic fibers during isothermal treatments in air under constant loads were measured by using a differential transformer. A static tensile load was applied to a yarn specimen at room temperature, and the initial gage length l_0 was determined. Then, the specimen under the load was inserted into an oven, and the specimen length l was measured during heat treatment as a function of heat treatment time. The temperature in the oven was controlled with a precision of $\pm 1^\circ\text{C}$. In this paper the extension or contraction of the acrylic fibers during heat treatment is represented by the length change ratio λ_l , which is defined as follows:

$$\lambda_l = l/l_0$$

The applied stress was calculated per unit area of the original cross-sectional area of a specimen before heat treatment. The original cross-sectional area was calculated from the linear density and density of the fibers.

Elemental Analysis. Elemental analysis was carried out with a Yanagimoto Model MT-2 CHN Corder. Oxygen values were determined by difference.

Density. Densities were measured at 25°C according to the density gradient column method. An *n*-heptane-carbon tetrachloride density gradient column was used to measure densities from 1.10 to 1.50 g/cm³. For the measurement of densities from 1.50 to 1.60 g/cm³ a density gradient column prepared from an *n*-heptane-carbon tetrachloride-ethylene dibromide mixture was adopted.

Wide Angle X-Ray Diffraction. The X-ray diffraction measurements were made with a Rigaku Denki diffractometer using Ni-filtered $\text{CuK}\alpha$ radiation. The X-ray beam was directed to a heat-treated fiber specimen perpendicularly to its fiber axis, and the equatorial diffraction intensity at the Bragg angle $2\vartheta = 17.0^\circ$, which is due to the polyacrylonitrile crystallite, and the diffraction at $2\vartheta = 25.5^\circ$, which is due to the cyclized polymer structure, were measured. From

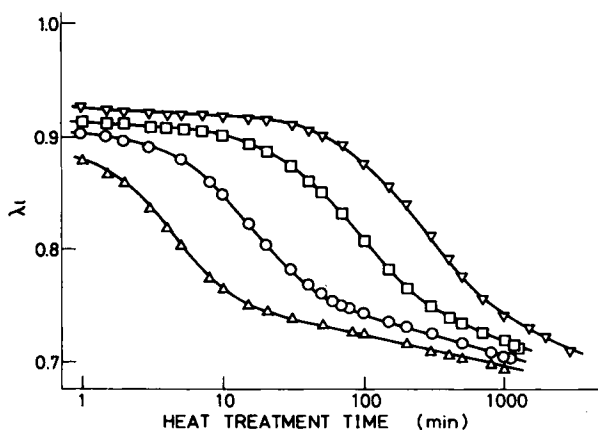


Fig. 1. Variation of the length change ratio λ_l during heat treatment of acrylic fibers at various temperatures ($^{\circ}\text{C}$) in the free state: (∇) 208; (\square) 225; (\circ) 252; (Δ) 270.

the intensity distributions were measured the maximum intensity I_p of the arc at $2\vartheta = 17.0^{\circ}$, the maximum intensity I_c at $2\vartheta = 25.5^{\circ}$, and the half-width X_h of the intensity distribution of the arc at $2\vartheta = 25.5^{\circ}$ at half-maximum intensity.

The "aromatization index" described by Uchida et al.¹¹ was calculated from the following equation:

$$\text{aromatization index} = I_c / (I_c + I_p)$$

As a measure of the orientation of the cyclized polymer structure, the orientation parameter was calculated according to the description adopted by Farrow and Bagley¹² as follows:

$$\text{orientation parameter} = (90^{\circ} - \varphi^{\circ}) / 90^{\circ}$$

where $\sin \varphi = \cos \varphi \sin(X_h/2)$, and the angle $90^{\circ} - \varphi^{\circ}$ corresponds to the angle between the normal φ and the fiber axis.

RESULTS AND DISCUSSION

Length Changes

Figure 1 shows the variation of the length change ratio with heat treatment time, measured at various temperatures under the minimum applied stress required to keep a specimen straight during heat treatment. The state of specimen during heat treatment under the minimum applied stress is denoted as the free state. When a specimen in the free state was inserted into the oven at a constant temperature, the specimen instantaneously developed a certain value of contraction. Then, the specimen increased contraction gradually with increasing heat treatment time.

The length change curves in Figure 1 have some common characteristics independently of temperature. The fibers first contract at a slower rate against the logarithmic heat treatment time. After a lapse of time the fibers begin to increase the contraction rate, and the contraction rate reaches a maximum at

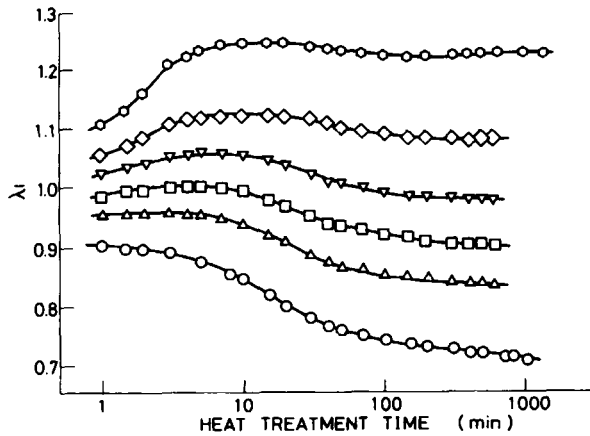


Fig. 2. Variation of the length change ratio λ_l during heat treatment of acrylic fibers at 252°C under various applied stresses (MN/m^2): (○) free state; (Δ) 2.87; (□) 5.03; (▽) 7.18; (◇) 9.43; (○) 11.38.

a certain heat treatment time. Then the fibers decrease the contraction rate and become to contract almost at a constant rate at longer times.

Figure 2 shows the length change curves obtained under various applied stresses at 252°C. The fibers broke in the earliest period of heat treatment time under an applied stress larger than about 11.4 MN/m^2 .

As is found in Figure 2, the influence of applied stress on length change is prominent in the period between the onset of heat treatment and about 8 min. The length change in this period changes from contraction to extension with increasing applied stress. Under higher applied stresses, the fibers develop instantaneously a certain extension on heating and then extend gradually with increasing heat treatment time. Under intermediate applied stresses, the fibers initially contract and then extend gradually.

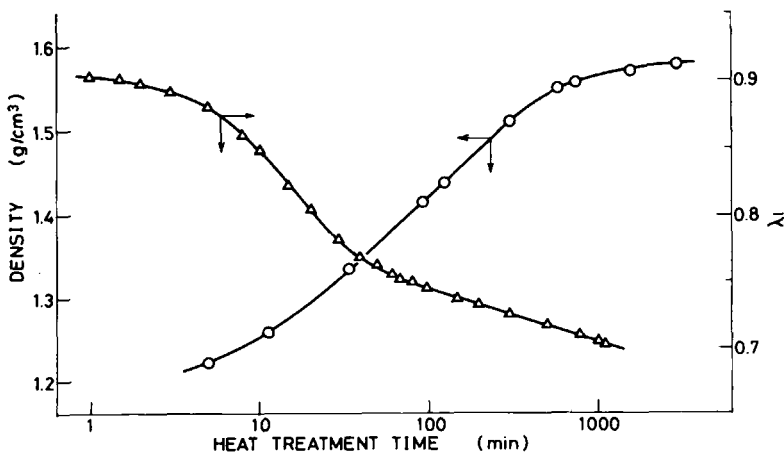


Fig. 3. Variation of density during heat treatment of acrylic fibers at 252°C (○). Variation of the length change ratio λ_l measured for the fibers at 252°C in the free state is also shown for comparison (Δ).

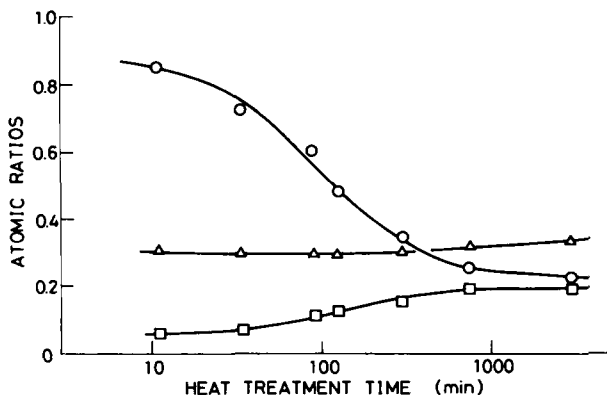


Fig. 4. Variation of the atomic ratios in number of hydrogen (O), nitrogen (Δ), and oxygen (\square) against carbon during heat treatment of acrylic fibers at 252°C.

It is noted that at longer times than about 8 min after starting heat treatment the fibers under various applied stresses represent a contractive behavior basically similar to that observed in the free state, the fibers contracting first at a faster rate and then at a slower rate against the logarithmic heat treatment time.

Structural Changes

Figure 3 shows the variation of density with heat treatment time for the fibers heat-treated at 252°C in the fixed state on a frame. The density of the original fibers was 1.18 g/cm³. In Figure 3 the density increases with increasing heat treatment time and approaches a constant value of about 1.58 g/cm³ at longer times.

In Figure 4 the atomic ratios in number of hydrogen, nitrogen, and oxygen against carbon, which were calculated from the elemental analysis of the heat-treated fibers, are plotted against heat treatment time. The hydrogen and

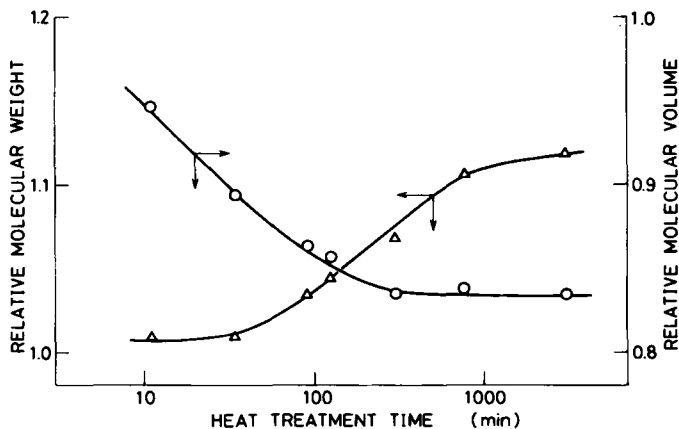


Fig. 5. Variations of the relative molecular weight (Δ) and relative molecular volume (O) per repeat unit during heat treatment of acrylic fibers at 252°C.

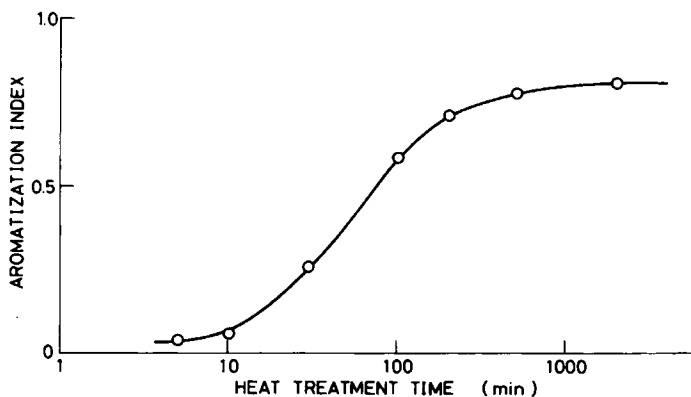


Fig. 6. Variation of aromatization index during heat treatment of acrylic fibers at 252°C.

oxygen ratios change with heat treatment time; in contrast, the nitrogen ratio keeps approximately a constant value. This indicates, as pointed out by Standage et al.,¹³ that any chain scission occurring during the reaction largely results in the removal of whole number multiples of acrylonitrile units.

From Figures 3 and 4 it is found that the contractive length change is closely related to the changes of density and elemental composition; the length change ratio, the density, and the atomic ratios of hydrogen and oxygen greatly varying in the range approximately between 8 and 80 min of heat treatment time on the logarithmic scale. These facts indicate that the length contraction—except the instantaneous component appearing at the earliest period of heat treatment—was developed due to thermodegradative changes in the fiber structure.

By assuming that the original and heat-treated fibers have three carbon atoms per repeat unit on average, the molecular weight and molecular volume per repeat unit were calculated from elemental compositions and densities. The results are shown in Figure 5 where the relative molecular weight denotes the ratio of the molecular weight per repeat unit for the heat-treated fibers against that for the original fibers, and the relative molecular volume denotes the ratio of the molecular volume per repeat unit for the heat-treated fibers against that for the original fibers. The increase of the relative molecular weight with heat treatment reaches finally about 11%, while the relative molecular volume decreases by about 17%. As a consequence, the density increases by about 34%.

In Figure 5 the change of the relative molecular weight seems to lag behind that of the relative molecular volume. It is estimated that the density increase at shorter heat treatment times is contributed by the volumetric contraction rather than the oxygen uptake and at longer times by the oxygen uptake rather than the volumetric contraction.

Figure 6 represents the plots of the aromatization index vs. the logarithmic heat treatment time for the fibers heat-treated at 252°C in the fixed state. The X-ray diffraction at the Bragg angle $2\theta = 25.5^\circ$, which is newly developed for acrylic fibers heat-treated in air, is diffuse at the stage of this heat treatment. However, during the carbonizing treatment of acrylic fibers preliminarily heat-treated in air, the diffraction at $2\theta = 25.5^\circ$ sharpens considerably and approaches to the spacing of turbostratic graphite. From this Miyachi et al.¹⁴ have considered that the planar cyclized segments formed by the additional poly-

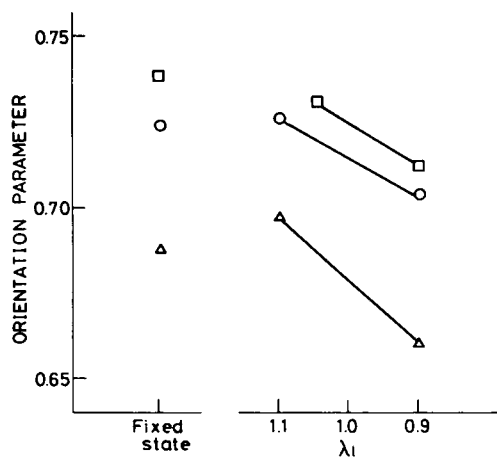


Fig. 7. Orientation parameter for acrylic fibers heat-treated in the fixed state and under various applied stresses. The orientation parameter for the fibers heat-treated under various applied stresses is plotted against the length change ratio λ_l at corresponding heat treatment time. Heat treatment temperature ($^{\circ}\text{C}$) and time (min); (□) 225, 700; (○) 252, 200; (Δ) 270, 80.

merization of the nitrile side groups during heat treatment are built up and construct a stacking which has a separation similar to that of graphite planes. The aromatization index may be assumed as an index representing the extent of the stacking of the cyclized segments. It is considered that the decrease of the relative molecular volume is due to the stacking of the cyclized segments since the decrease of the relative molecular volume with heat treatment in Figure 5 is closely related to the increase of the aromatization index in Figure 6.

Lateral Contraction and Orientation

In order to study the effect of mechanical conditions imposed on acrylic fibers during heat treatment on the orientation of the stacking of cyclized segments, the orientation parameter was determined for the fibers heat-treated in the fixed state and under constant applied stress at three different temperature-time conditions; at 225°C for 700 min, at 252°C for 200 min, and at 270°C for 80 min. As is found in Figure 1, the acrylic fibers exhibit a constant value of $\lambda_l = 0.73$ if they are heat-treated in the free state at these three temperature-time conditions, respectively. The results obtained are shown in Figure 7, where, with the fibers heat-treated under constant applied stresses, the orientation parameter is plotted against the length change ratio λ_l at corresponding heat treatment time.

In Figure 7 the relation between the orientation parameter and the length change ratio for the fibers heat-treated under constant applied stresses shows that the higher the length change ratio, the higher the orientation of the cyclized segments if heat treatment temperature is constant. This feature indicates that the extension of polyacrylonitrile chains in the earliest period of heat treatment strongly influences the development of the orientation of the cyclized segments, since the extension during heat treatment under a constant applied stress occurs in the earliest period, and in the later period the fibers tend to contract even when the fibers are subjected to higher applied stresses. However, it is also known from Figure 7 that the orientation of the cyclized segments for the fibers heat-treated in the fixed state has a high value comparable with that for the fibers

extended during heat treatment under a constant applied stress. Therefore, the orientation of polyacrylonitrile chains before the cyclization proceeds is not a unique factor determining the orientation of the cyclized segments. It is considered that the high orientation observed for the fibers heat-treated in the fixed state relates to the fact that the length contraction which is commonly developed in the later period of heat treatment under constant applied stresses is not allowed to occur with the heat treatment in the fixed state.

The fact that the fibers heat-treated in the fixed state gave a high orientation of the cyclized segments can be explained by considering the interaction of external constraint and volume contraction which occurs during heat treatment. When the stacking of the planar cyclized segments is formed, a volume which is occupied by a group of cyclized segments may show a large contraction in the direction in which the planar cyclized segments are built up. As is known from the experimental result that the fibers contract in the later period of heat treatment under high applied stresses, the volume contraction accompanies a high contractive stress. The length contraction cannot be restrained enough by an applied stress which is closer to the one leading the fibers to fracture in the earliest period of heat treatment. With the heat treatment in the fixed state, the fibers are allowed to contract only in the direction perpendicular to the fiber axis. The cyclized segments, therefore, should be built up perpendicularly to the fiber axis to attain a required volume contraction. Consequently, during heat treatment the cyclized segments become preferentially oriented parallel to the fiber axis. In contrast, in the case that the fibers are able to contract more or less longitudinally during heat treatment, the stress restricting the direction of the building up of the cyclized segments is smaller than that acting in the heat treatment in the fixed state. Therefore, with the heat treatment under constant applied stresses, even when the fibers are extended in the earliest period of heat treatment, the additional extension of polyacrylonitrile chains will not be transferred effectively to the orientation of the stacking of the cyclized segments.

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