

Thermal Shrinkage Behavior of Preoxidized Polyacrylonitrile Fibers During Carbonization

ZONGQUAN WU, DING PAN, XIAOBO FAN, and BAOJUN QIAN,
*Man-Made Fiber Research Institute, China Textile University,
Shanghai, China*

INTRODUCTION

The preparation of carbon fibers from polyacrylonitrile (PAN) by the usual process consists of two steps: one is the preoxidation of the fibers below 300°C in ordinary atmosphere causing the fiber to assume the partially cyclized trapezoid structure; the other is the carbonization of the fibers at high temperature which yields high-strength, high-modulus carbon fibers with a turbostratic graphite structure. There are many publications on the thermal shrinkage behavior of PAN fibers during preoxidation,¹⁻⁵ but only few papers on the thermal behavior of preoxidized fibers during carbonization.^{6,7} Knowledge about the thermal shrinkage stress and thermal shrinkage modulus of fibers in the process of carbonization is still lacking; the present paper aims at making up some of these deficiencies.

Differential scanning calorimetry (DSC) was performed at constant length and under free shrinkage to yield apparent activation energies.

EXPERIMENTAL

Samples

Preoxidized PAN fiber with a composition: AN : IA = 98.5 : 1.5, IA-Itaconic acid.

Spinning method: One step HNO₃ method.

Preoxidation: Continuous, at a final temperature of 280°C in ordinary atmosphere.

Degree of preoxidation: 73% (measured by DSC).

$$CD\% = 1 - \frac{\Delta H_{PF}}{\Delta H_F} \cdot 100$$

where CD% is the degree of cyclization of the preoxidized fibers, ΔH_{PF} is the cyclization heat of the original preoxidized fibers in nitrogen, and ΔH_F is the cyclization heat of the original fiber in nitrogen.

Apparatus and Method for Measuring Thermal Shrinkage

The experimental apparatus shown in Figure 1 is a self-made, high temperature carbonization oven. A linear heating program with an adjustable heating

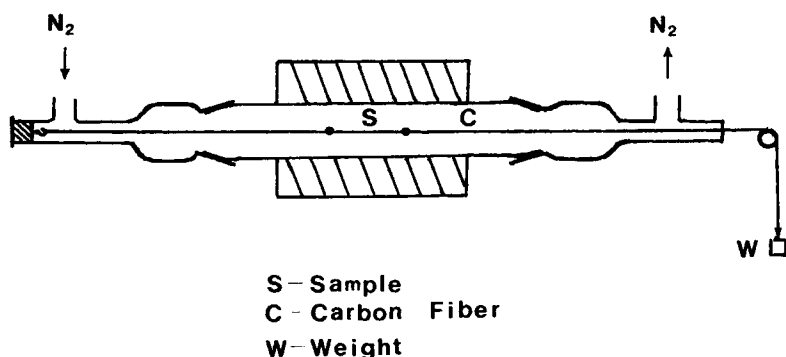


Fig. 1. Schematic diagram of the apparatus used for carbonization.

rate in the range of 5–20°C/min was used, a heating rate of 10°C/min is generally used. A 10 cm length of sample in the oven is tied on both ends on loops of carbon filament yarns; the loops are then led out of the oven. The change in length is measured by displacing a sliding electric resistance sensor, the voltage output of which is recorded on a potentiometric recorder. The measurable displacement range is from 0.15 to 20 mm. Nitrogen is used for protection.

Differential Scanning Calorimetry (DSC)

Instrument: Thermal Analyzer of Type 900, Du-Pont Co. USA.

Weight of sample: 3.00 ± 0.01 mg.

Temperature range: 100–650°C, Heating rate: 10°–50°C/min.

Protection gas: high purity nitrogen, 120 mL/min.

Sampling: fiber was wound around a piece of aluminum at constant length.

EXPERIMENTAL RESULTS AND DISCUSSION

Thermal Shrinkage Behavior of the Preoxidized PAN Fibers

The thermal shrinkage curves of the fibers were determined in the temperature range of 100 to 1200°C under tensions of 7–70 mg/d. A set of shrinkage curves is shown in Figure 2. The shape of the curves bears some resemblance to that of the original precursor. From these, it can be seen that thermal shrinkage exists always during the entire process of carbonization of the preoxidized PAN fibers in the region of 100–1200°C. However, in the different temperature regions, the extent of thermal shrinkage varies greatly. The whole process can be divided into three temperature regions:

1. At temperatures below 500°C, the thermal shrinkage behavior of the fiber is greatly affected by tension, heating rate, and degree of preoxidation.⁸ It is known that PAN fiber is composed of linear C—C chain macromolecules with polar side groups —CN attached to them. After preoxidation some of the side groups undergo cyclization, forming a partly cyclized ladder structure. In this stage, thermal shrinkage results from entropic shrinkage and further cyclization of the uncyclized segments of the macromolecules. Tension will restrict the entropic shrinkage and even extend the coiled macromolecules; so, at the

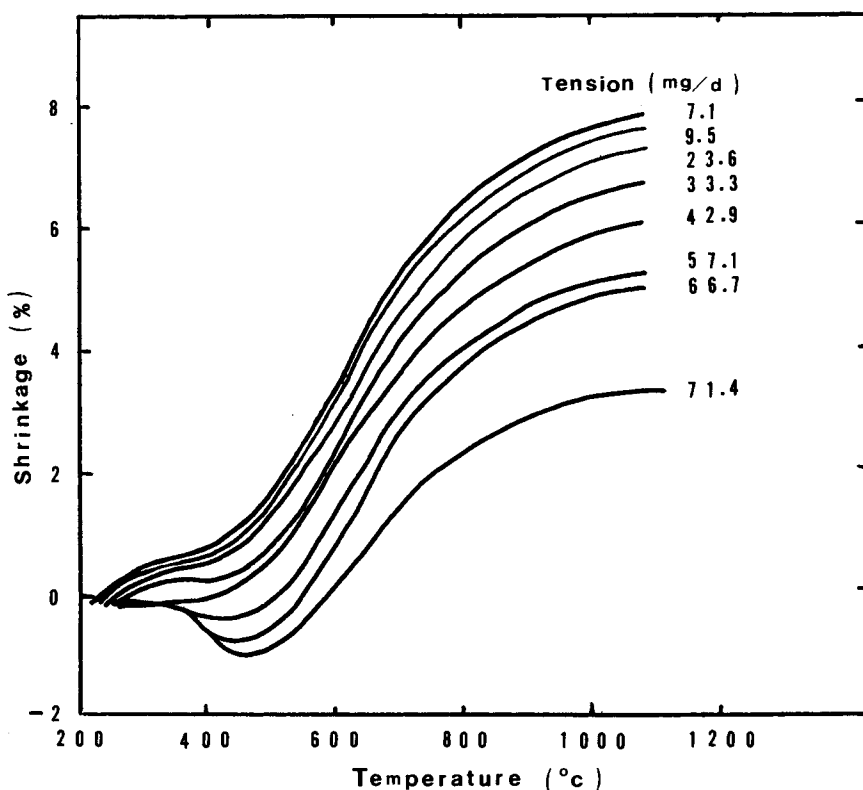


Fig. 2. Thermal shrinkage behavior of preoxidized PAN fiber during carbonization under different tension.

initial stage of carbonization the thermal shrinkage of the fiber decreases as tension is increased. At a tension higher than 43 mg/d, there is almost no shrinkage. Further increase in tension will even elongate the fiber.

2. In the temperature region between 500 and 800°C, relatively large shrinkage of the fiber occurs which is less affected by degree of preoxidation and condition of carbonization. In this temperature region the total shrinkage of the fiber is nearly constant, about 4–4.5% as can be seen from the data in Table I.

The results of elemental analysis and density determination (using NaI solution by flotation method) of the preoxidized PAN fiber during carbonization are shown in Figures 3 and 4. It can be seen that in the region of 500–800°C, the macromolecules of the fiber are losing noncarbon elements through ejection of small gaseous molecules like H_2O , HCN , NH_3 , N_2 , CO_2 ,

TABLE I
Thermal Shrinkage of Preoxidized PAN Fiber During Carbonization
in the Temperature Region of 500–800°C Under Various Tensions

Tension (mg/d)	7.1	9.5	23.8	33.3	42.9	57.1	66.7	71.4
Thermal shrinkage (%)	4.3	4.4	4.3	4.4	4.1	4.2	4.1	3.5

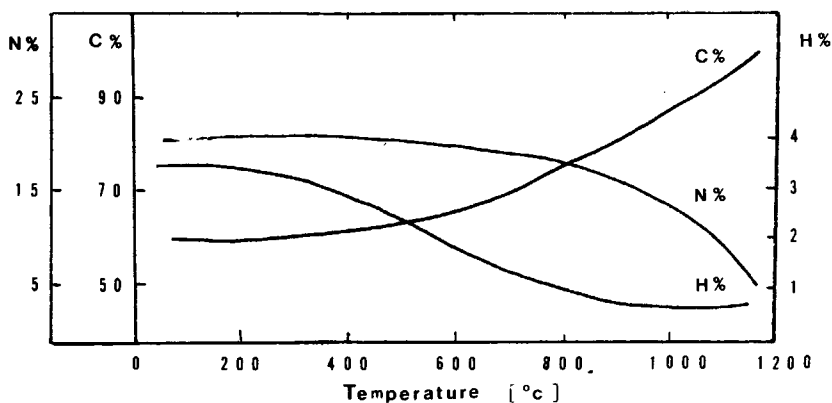


Fig. 3. The elemental analysis of preoxidized PAN fiber during carbonization.

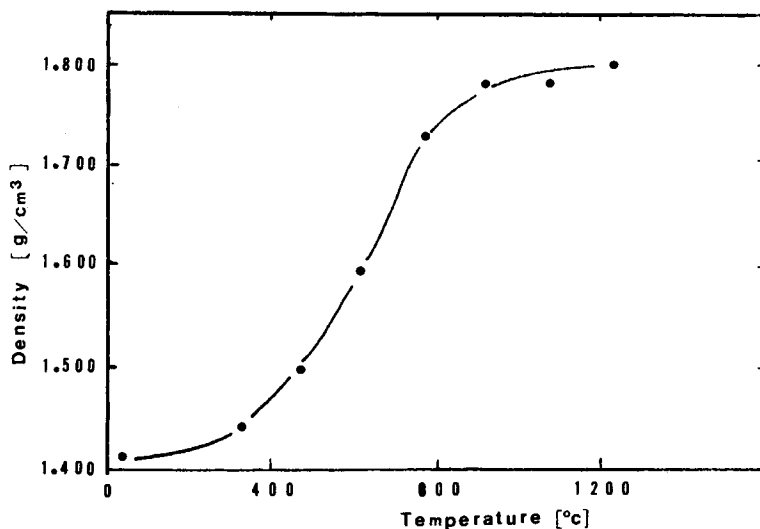


Fig. 4. The density of preoxidized PAN fiber during carbonization.

CO, etc. and undergo rearrangement and crosslinking, which results in the thermal shrinkage of the fiber. In this region the thermal shrinkage of the fiber is less affected by tension and heating rate and the reaction is dominated by the rate of pyrolysis. In an inert atmosphere, pyrolysis is mainly influenced by temperature. Once free radicals are formed through pyrolysis, the crosslinking reaction occurs rapidly, as shown by the rapid rise of modulus (see Fig. 6 below).

3. At temperatures above 800°C, the thermal shrinkage of the fiber is much less. From Figure 4 it can also be seen that in this region, the density of the fiber gradually levels off. Further intermolecular crosslinking takes place with the elimination of N₂ and HCN. Macromolecules form a planar structure with rather large size and high rigidity. Therefore, the relative movements of the macromolecular segments become very difficult, leading to a marked drop in the degree of thermal shrinkage.

Thermal Shrinking Stress and Thermal Shrinkage Modulus of the Preoxidized PAN Fibers During Carbonization

From a plot of tension vs. shrinkage, a linear relation can be deduced (Fig. 5), and a thermal shrinking stress and modulus of the fiber can be calculated.

We denote the real shrinkage as Δl_0 . Let the external force be F and the creep compliance $J(T)$, the creep Δl_c will be given by:

$$\Delta l_c = FJ(T) \quad (1)$$

The apparent thermal shrinkage Δl_a should be

$$\Delta l_a = \Delta l_0 - \Delta l_c = \Delta l_0 - FJ(T) \quad (2)$$

At constant temperature (T), a linear relationship between Δl_a and tension F exists (Fig. 5). Hence the real thermal shrinkage may be obtained by extrapolating the straight line to $F = 0$,

$$\Delta l_0 = \lim_{F \rightarrow 0} \Delta l_a \quad (3)$$

Also, the force for completely preventing shrinkage can be obtained as

$$F_0 = \lim_{\Delta l_a \rightarrow 0} F \quad (4)$$

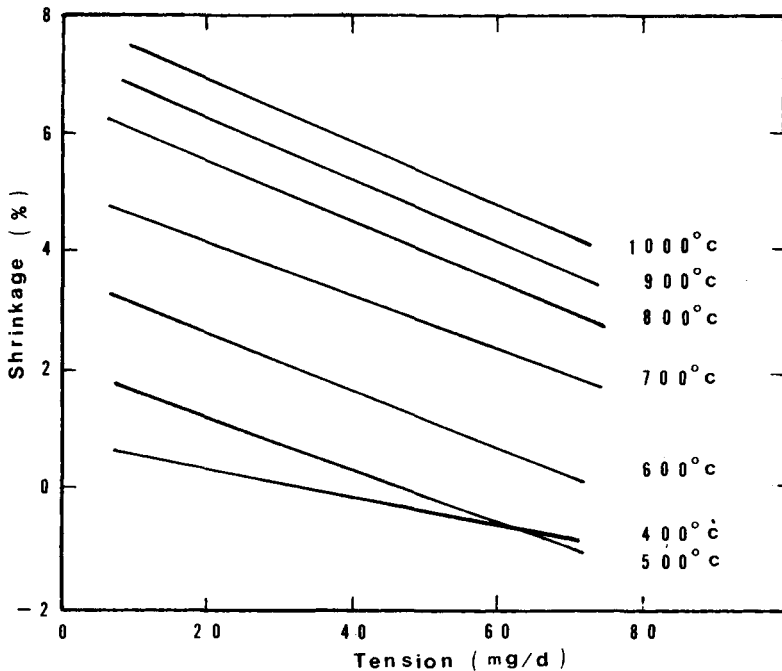


Fig. 5. Tension vs. shrinkage of preoxidized PAN fiber during carbonization at different temperature.

Thus, the thermal shrinking stress $\sigma_s(T)$ and thermal shrinkage modulus $E_s(T)$ of the fiber during carbonization are:

$$\sigma_s(T) = F_0/A = \lim_{\Delta l_a \rightarrow 0} (F/A) \quad (5)$$

$$E_s(T) = \frac{\sigma_s(T)}{\Delta l_0(T)/l_0} \quad (6)$$

It should be pointed out that during carbonization the thermal weight loss of the fiber attains a value of about 40%, the fiber density increases greatly and a big reduction in the cross section of fibers takes place. This must be taken into account in calculating the stress and modulus of the fiber. By observing the fiber diameter with a microscope and taking full consideration of the effects of temperature and tension on the cross-section of the fiber, we obtained the cross-section of the fiber at different temperature and given tension. Based on that, the thermal shrinking stress and modulus of the fiber were obtained as illustrated in Figure 6, it shows that at increasing temperature the thermal shrinkage stress increases continuously, the thermal shrinkage modulus decreases first, reaches a minimum at 550°C, and then increases again as temperature increases further. The changes of thermal shrinkage modulus correspond to the development of fiber structure. At the beginning, the macromolecules exist mainly as a linear ladder structures, then turn into a planar structure and finally form a turbostratic graphite-structure. It is obvious that during carbonization when the temperature is below 600°C the control of tension is of importance.

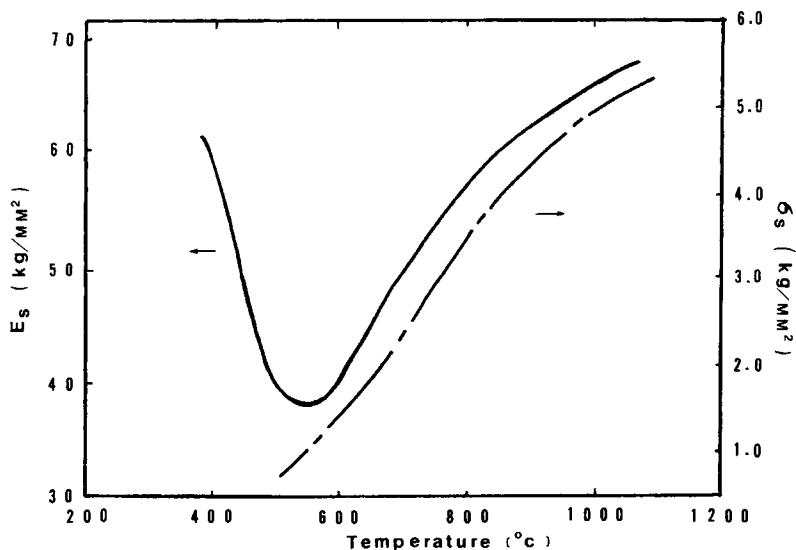


Fig. 6. Thermal shrinkage stress and thermal shrinkage modulus of preoxidized PAN fiber during carbonization.

THE EFFECT OF TENSION ON THE KINETICS OF CARBONIZATION

DSC curves of preoxidized PAN fibers taken at constant length and under free shrinkage are shown in Figures 7 and 8. The apparent activation energies of the initial carbonization obtained by the Kissinger method⁹ are listed in Table II. It can be seen that the apparent activation energy of carbonization at constant length is lower than that under free shrinkage. This indicates that tension plays an important role in promoting carbonization.

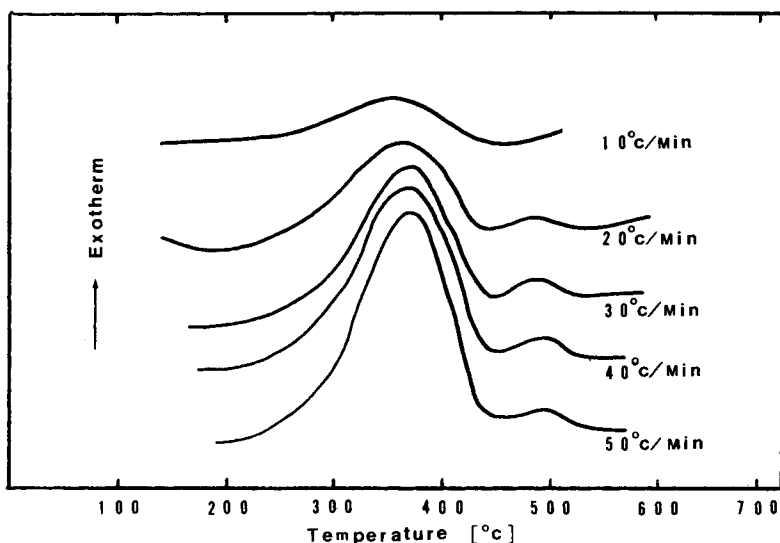


Fig. 7. DSC curves of preoxidized PAN fiber under relaxed conditions.

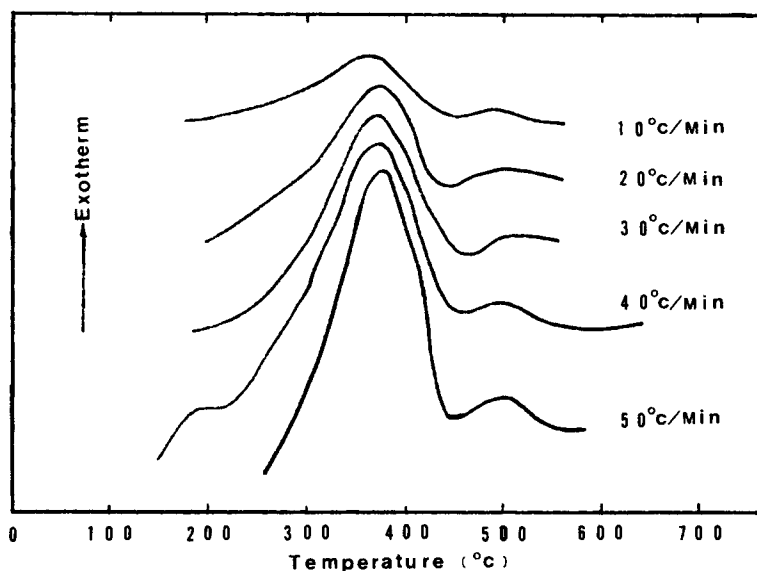


Fig. 8. DSC curves of preoxidized PAN fiber under constant length.

TABLE II
Kinetic Parameters of Preoxidized PAN Fiber by DSC

	Heating rate $B(^{\circ}\text{C}/\text{min})$	Temperature		$1_n(B/T_m^2)$	$1/T_m \times 10^3$	Apparent activation energy $E_a(\text{kcal}/\text{mol})$
		$t_m(^{\circ}\text{C})$	$T_m(^{\circ}\text{K})$			
Under free relaxation	10	350.6	623.6	-10.568	1.604	54.1
	20	360.1	633.1	-9.906	1.580	
	30	364.1	637.1	-9.513	1.570	
	40	369.5	642.5	-9.242	1.554	
	50	373.8	646.8	-9.032	1.546	
At constant length	10	345.7	618.7	-10.553	1.616	42.9
	20	359.0	632.0	-9.902	1.582	
	30	363.5	636.5	-9.511	1.571	
	40	369.7	642.7	-9.292	1.556	
	50	374.5	647.5	-9.034	1.544	

CONCLUSIONS

The thermal shrinkage process of preoxidized PAN fiber during carbonization (at a tension of 7–70 mg/d and heating rate of 10°C/min) can be divided into three regions. Below 500°C, tension, heating rate, and thermal history have great effects. Between 500 and 800°C little effects of these parameters are observed (a constant shrinkage of 4–4.5%). Above 800°C, thermal shrinkage reaches a limiting value. These three regions correspond to the development of different fiber structures, that is, the formation of a cyclized ladder structure, planar structure, and turbostratic graphite-structure.

The stress and modulus of thermal shrinkage can be deduced from the thermal shrinkage curves. At increasing temperature the thermal shrinking stress increases continuously, the thermal shrinkage modulus decreases first, reaches a minimum at 550°C, and then increases again. During carbonization the control of tension below 600°C is of great importance.

DSC curves of preoxidation of PAN fiber at constant length and under free shrinkage are obtained. The apparent activation energy of carbonization at constant length is less than that under free shrinkage. The tension control plays an important role during carbonization.

References

- O. P. Bahl and L. M. Manocha, *Angew. Macromol. Chem.*, **48**, 145–159 (1975).
- E. Fitzner and D. J. Muller, *Angew. Makromol. Chem.*, **144**, 117–133 (1971).
- Baojun Qian, Zhan Sun, Chengxun Wu, and Hongjiang Tian, *Rev. Polym. Engr.*, to appear (1985).
- A. Takaku and T. Kobayashi, *Fiber Sci. Tech.*, **15**, 87–98 (1981).
- L. M. Manoch and O. P. Bahl, *Fiber Sci. Tech.*, **13**, 199–212 (1980).
- L. M. Manoch, et al., *Angew. Makromol. Chem.*, **67**, 11–29 (1978).
- O. P. Bahl and L. M. Manocha, *Fiber Sci. Tech.*, **12**(2), 31–39 (1979).
- Zongquan Wu, Ding Pan, Xiaobo Fan, and Baojun Qian, in preparation.
- H. F. Kissinger, *Anal. Chem.*, **29**, 1702 (1957).

Received August 4, 1986

Accepted September 23, 1986