Aspects on Prestretching of PAN Precursor: Shrinkage and Thermal Behavior

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ABSTRACT: Polyacrylonitrile (PAN) fibers of a special grade have been modified by a method of prestretching with various stretching ratios from negative to positive before the onset of stabilization. The effect of such pretreatments on the thermorhelogical and thermal behaviors of PAN fibers was followed by free shrinkage experiments and differential scanning calorimetry (DSC) analyses. It was found that prestretching had a significant influence on the physical shrinkage of PAN fibers. DSC results of PAN fibers showed dependence not only on atmospheric conditions but also on the extent of prestretching. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67:** 1185–1190, 1998

Key words: polyacrylonitrile fibers; prestretching; free shrinkage; thermal behavior

INTRODUCTION

It has been well established that polyacrylonitrile (PAN) fiber is one of the most suitable and widely used precursors for making high-performance carbon fiber.[1–3] When PAN fibers are subjected to heat treatment at temperatures higher than 180°C, they undergo characteristic shrinkage.[4–6] This shrinkage leads to the relaxation of the molecular orientation of PAN fibers and thus deteriorates the mechanical properties of the resulting carbon fibers. Therefore, for obtaining high-quality carbon fibers, restraint on the shrinkage, or even stretching during the oxidation stage of PAN fibers, is imperative and has actually been widely used in the industry of carbon fiber production. The shrinkage of PAN fibers on the oxidation temperature region was considered to consist of two distinct processes involving, respectively, a physical and a chemical mechanisms.[4–7] So, the overall shrinkage was classified into two categories: physical shrinkage and chemical shrinkage, or initial shrinkage and secondary shrinkage. It was observed in air that an increase in the linear heating rate caused higher intensity of secondary shrinkage.[8] This result was qualitatively attributed by Fitzer et al.[8] to a contribution from intermolecular crosslinking reactions, which were presumed to occur at a higher extent at increasing rates. Stimulated by this observation, a set of experiments on the free shrinkage behavior of PAN fibers under different linear heating rates not only in air but also in argon were then conducted. It was found that with an increase in linear heating rates, the amount of secondary and total shrinkage was markedly increased under both atmospheres. In addition, the ultimate extent of shrinkage of PAN fibers in argon was quite comparable to that in air at the same heating rate. These results attempted to show that in the progression of secondary shrinkage, in addition to the purely chemical reaction-induced shrinkage, which caused a limiting shrinkage of about 30%,[9] there might be a physical process, namely, the morphological transformations, which includes a progressive "melting" of ordered domains ensued by entropic relaxation of these domains. From this point, it was therefore postulated that inducing

Table I   Prestretching Ratios on PAN Fibers

Sample Code	A	B	C	D	E	F
Prestretching ratio (%)	−20	−10	0	10	20	30

different orientation and order in the original PAN fiber might have an influence on the progression of the thermorheological response, and even the thermal reaction behavior,[10] of PAN fibers during the oxidative temperature region. To this end, a method of prestretching was used to alter the orientation and order of the PAN precursor. The fibers with such modification were then followed by their free shrinkage behavior and thermal analysis. The results, together with the aforementioned free shrinkage behavior of PAN fibers under different heating rates, are reported here.

EXPERIMENTAL

A special grade of PAN fibers (Courtelle fiber; Courtaulds Ltd., United Kingdom) with 3,000 filaments and 1.22 dtex has been used as the precursor. Prestretching treatment of the fibers was carried out on the prestabilization (or preoxidation) furnace in the carbon fiber line of our laboratory[2] in a continuous way. The temperature was kept at 170°C while the stretching ratio was varied from −20 to 30%, i.e., 20% shrinkage to 30% stretch. The correspondence of sample code with stretching ratios is given in Table I.

Free shrinkage experiments were performed within a vertical quartz furnace. The heating rate was achieved by carefully controlling and adjusting the heating electric voltage. The correspondence between electric voltage and heating rate was carefully monitored and measured with a thermocouple prior to the experiment.

Thermal analyses of fibers in nitrogen and in air were carried out on a Dupont model 1090 thermal analyzer. The heating rate was chosen at 5°C/min.

RESULTS AND DISCUSSION

Free Shrinkage Behavior of PAN Precursor Under Different Heating Rates

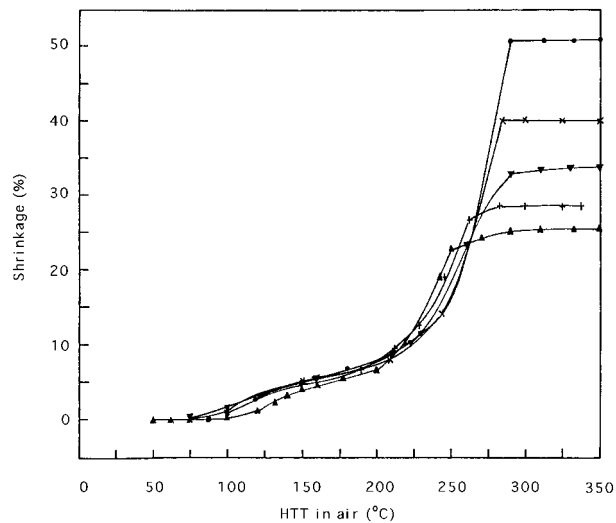The free shrinkage behaviors of virgin PAN precursor fibers under dynamic heating conditions in

Figure 1   Free shrinkage behavior of PAN fibers under linear heating treatment in air: (▲) 1°C/min; (+) 3°C/min; (▼) 5°C/min; (×) 7.5°C/min; (●) 10°C/min.

air and in argon are shown in Figures 1 and 2, respectively. Curves in both figures indicate that increasing the heating rate had a significant effect on the amount of secondary shrinkage and the total amount of shrinkage. That is, with an increase in the heating rate, the amount of secondary and total shrinkage is markedly increased under both atmospheres. Comparatively, the entropic shrinkage due to the relaxation of molec-
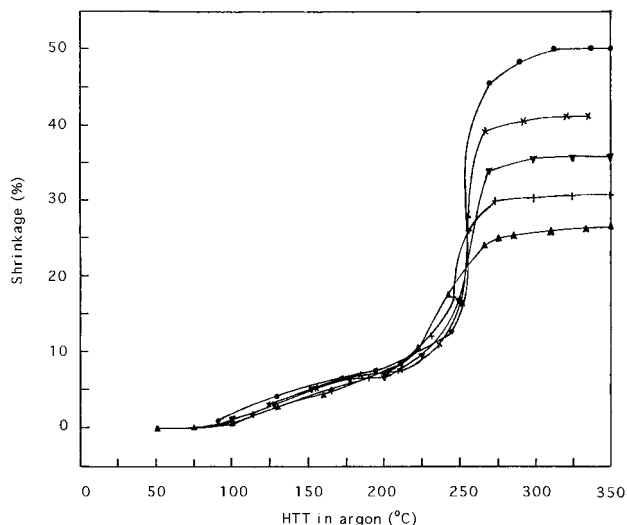

Figure 2   Free shrinkage behavior of PAN fibers under linear heating treatment in argon: (▲) 1°C/min; (+) 3°C/min; (▼) 5°C/min; (×) 7.5°C/min; (●) 10°C/min.
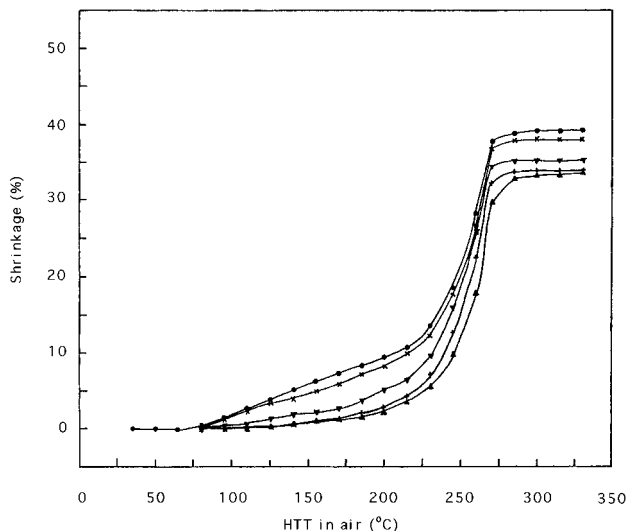
Figure 3 Free shrinkage behavior of pretreated PAN fibers in air: (▲) A; (+) B; (▼) C; (×) D; (●) F. Heating rate: 7.5°C/min.

ular chains in the disordered phase of PAN fibers was not largely affected by either the heating rate[8] or the ambient atmosphere. In addition, the ultimate extent of shrinkage of PAN fibers in argon is quite comparable to that in air at the same heating rate. In the medium of argon, the contributions from dehydrogenation, aromatization, and intermolecular crosslinking via the elimination of water due to oxygen attack and introduction, which have been considered to be an important part to the secondary and the final shrinkage, can be negligible. On the basis of these observations, it is tentatively conceived that during the region of secondary shrinkage of PAN fibers, in addition to the occurrence of pure reaction-induced chemical shrinkage, such as by cyclization, dehydrogenation, etc., there might also be a physical process, that is, reaction-induced morphological transformations. These morphological transformations include a progressive "melting" of ordered domains ensured by entropic relaxation of these domains. With an increase in heating rates, the rate and extent of these morphological transformations were increased because a higher rate of heat production was incurred at the reaction sites, due to the higher heating rate leading to a higher rate of reaction, and produced higher total shrinkage, as observed in Figures 1 and 2. Further studies of the structure characterization of PAN fibers on heat treatment under free shrinkage are in progress.

Effect of Prestretching on Shrinkage and Thermal Behavior of PAN Precursor

Figures 3 and 4 show the free shrinkages of prestretched PAN fibers in air and in argon atmospheres, respectively. The physical shrinkage (up to 180–200°C) of PAN fibers was primarily determined by the prestretching treatment. For those samples undergoing shrinkage during the pretreatment, the physical shrinkage was significantly reduced and could even be quenched. For samples stretched, however, the physical shrinkage was greatly increased. These variations in the physical shrinkage behavior of fibers are related to the rearrangements in the orientation of molecular chains of PAN fibers, especially in the disordered or less ordered portions, which were altered by stretching (or shrinkaging) during the pretreatment. That is, as has been reported,[11–13] when stretched, the orientation of molecular chains in the disordered regions was markedly improved; the improvement depended on the extent of stretching. Thus, during the temperature region of physical shrinkage, a higher extent of relaxation of these orientation-improved molecular chains in the disordered domains contributed to the observed higher extent of physical shrinkage, as shown in Figures 3 and 4. For those fibers undergoing shrinkage during the pretreatment, the orientation of molecular chains in the disordered domains was relaxed to some extent.[11,12] Thereafter, the physical shrinkage due to the re-
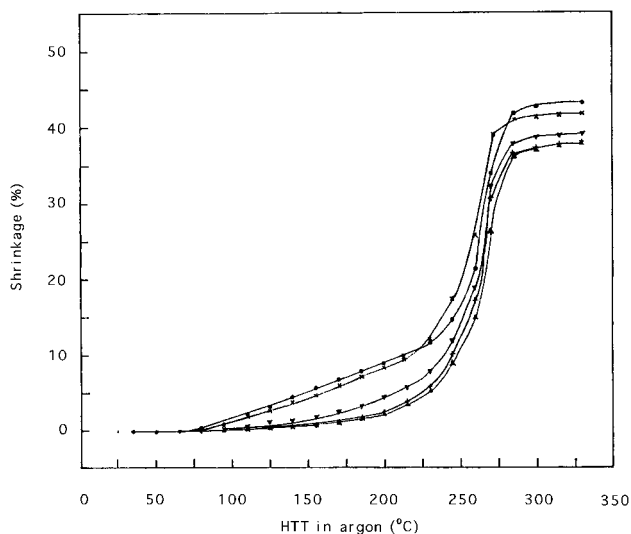

Figure 4 Free shrinkage behavior of pretreated PAN fibers in argon: (▲) A; (+) B; (▼) C; (×) D; (●) F. Heating rate: 7.5°C/min.
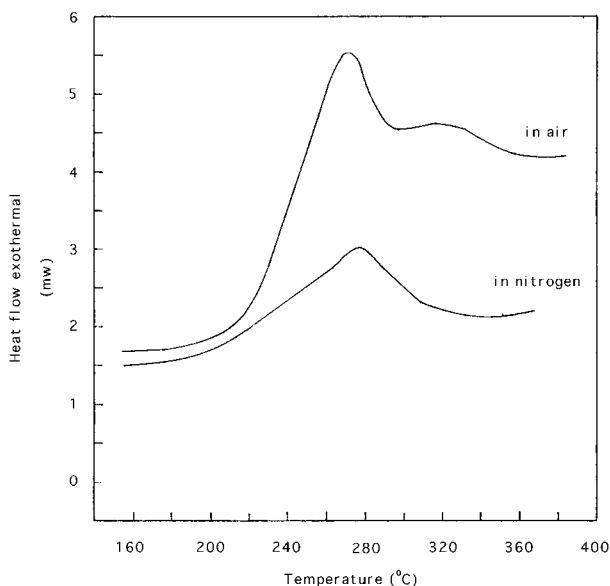
Figure 5 Typical DSC curves of pretreated PAN fibers (sample F).

laxation of orientation of these molecular chains was lessened.

In Figures 3 and 4, the overall shrinkage of fibers shows a corresponding trend with the physical shrinkages. That is, the amount of overall shrinkage increased with an increase in the stretching ratio. On the other hand, the extent of chemical shrinkage seemed not evidently affected by the pretreatment (either shrinkage or stretching). That is, the morphological rearrangements induced by the pretreatment did not appear to significantly influence the extent of secondary shrinkage. This appears to be the result of the nature of morphological rearrangements during the pretreatment, especially in the ordered fraction, to approximately the same levels in these fibers.[12] That is, the difference in the level of orientation and order of these laterally ordered portions among the pretreated PAN fibers was probably not so significant as to evidently affect the macroscale thermorheological response on the secondary shrinkage region of these fibers.

The effect of prestretching on the thermal reaction of PAN fibers was studied by differential scanning calorimetry (DSC). Typical DSC curves are given in Figure 5, showing the exothermic behavior of pretreated PAN fibers in air and in nitrogen. In the medium of air, despite a prominent exotherm peak around 270°C, which corresponds to the oxidative stabilization of PAN fibers, there appears a second peak, relatively broad and centered around 320°C. In the presence of nitrogen,

however, this second peak disappears. The appearance of this second exothermic peak in the air treatment of PAN fibers has been observed by Thomson[14] and Mathur et al.[15] and was qualitatively attributed to intermolecular crosslinking and aromatization of the cyclized structures during the thermal stabilization of PAN fibers.[15] Results from DSC measurements on those pretreated PAN fibers are given in Table II. The difference between the thermal behavior of PAN fibers in air and in nitrogen is dramatic, as shown in Table II. That is, the exothermic threshold and peak temperatures appear lower in the presence of air. Meanwhile, the total heat evolved during the stabilization is much higher in air treatment. Examination of the data in the presence of nitrogen in Table II appears to indicate that 1) the threshold and peak temperatures show a decreasing trend as the prestretching changes from negative, that is shrinkage (samples A, B, and C), to positive (samples D, E, and F); 2) the total heat, on the other hand, generally increases instead. For fibers stabilized in nitrogen, only cyclization occurs within the material. Thus, the decrease in threshold and peak temperatures, as from shrinkage to stretching during the pretreatment, suggests that, compared with shrinkage, the stretching on PAN fibers facilitated the cyclization. It has been reported that higher tension or stretch during the oxidative stabilization led to a higher value of aromatization index of PAN fibers, that is, a higher rate of cyclization.[16,17] Although the detailed mechanism accounting for this expediting effect of stretching, either before stabilization or during the stabilization, on the cyclization of PAN fibers is not fully understood, it may be due to the improvement in the orientation of the molecular chains along the fiber axis. Comparison of total heat production between samples of preshrinkage (A, B, and C) and those of prestretching (D, E, and F) indicates a higher amount of heat of the latter. Heat was produced by the cyclization of pendant CN groups of PAN fibers when treated in nitrogen. So, more heat evolution suggests more CN groups taking cyclization. In fact, prestretching improved the orientation of molecular chains not only in the ordered domains, but also and especially in the disordered domains.[11,12] This might bring more CN groups into a suitable position for cyclization and, therefore, lead to higher heat flow. On correlating the DSC results in the presence of air with the extent of prestretching, a general trend can be summarized, that is, with stretching increasing (including both

Table II DSC Results of Pretreated PAN Fibers

Sample Code	In Air			In Nitrogen		
	T_s^{a} (°C)	T_p^{a} (°C)	ΔH_{exo} (J/G)	T_s (°C)	T_p (°C)	ΔH_{exo} (J/G)
A	221.7	269.4	1,963	235.2	277.6	659
B	210.6	255.5	1,604	225.2	276.0	688
C	210.8	259.3	2,134	239.5	279.3	578
D	219.2	270.3	1,917	220.3	272.9	772
E	220.5	269.4	1,882	228.1	274.3	720
F	223.7	270.7	1,992	230.4	275.4	687

[a] T_s and T_p denote the exotherm start (or threshold) and peak temperatures, respectively.

from shrinkage to stretching and the stretching ratios), the threshold and peak temperatures shift toward a higher value, contrary to that in nitrogen and to that reported by Mathur et al.[18] Heat treatment of PAN fibers in air includes mainly two reactions, namely, cyclization and oxidation; the latter is triggered by the presence of oxygen. The lower threshold temperature in air than in nitrogen, as shown in Table II, clearly indicates that the presence of oxygen played a significant role in the initiation of cyclization, that is, the initiation of cyclization was eased by oxygen. Thus, it is inferred that the diffusion of oxygen into the reaction site would be important in determining the initiation of cyclization. Very probably, the improvement in the orientation and lateral order of molecular chains resulting from prestretching barricaded the diffusion of oxygen and, therefore, slowed down the initiation of cyclization, which resulted in an increase in threshold temperature. Similarly, the peak temperature is upshifted, as shown in Table II. Comparing the heat flow in air with that in nitrogen indicates that oxidation contributed more than cyclization to the total heat evolved in the stabilization of PAN fibers in air. That is, oxidation incurred more heat than cyclization. Oxidation took place by means of dehydrogenation and crosslinking. Meanwhile, oxygen was bonded to the molecular backbone in various groups. Dehydrogenation turned the cyclized structure into an aromatized structure, and crosslinking between molecular chains resulted in an increase in the size of the ladder structure. Both enhanced the stability of the structure of oxidized PAN fibers, that is, led to a decrease in potential energy, and, as a result, produced high heat, as indicated in Table II. Oxidation played a very significant role in the total heat flow of the oxidative stabilization of PAN fibers. The influence of morphological order variations, as induced by prestretching treatment on the heat flow, was therefore, markedly diluted and covered (Table II).

CONCLUSIONS

By conducting a series of free shrinkage experiments of PAN fibers under different linear heating rates and atmospheres, it was observed that increasing heating rates remarkably increased the amount of secondary shrinkage and total shrinkage, irrespective of the atmosphere. In addition, at the same heating rate, the total amount of shrinkage of PAN fibers in argon was quite comparable to that in air. A tentative mechanism, namely, morphological transformations, was proposed to account for the observed phenomenon. More detailed works on the structure characterization of PAN fibers under heat treatment remain to validate the proposal. Prestretching was found having a significant influnce on the physical shrinkage of PAN fibers. That is, the physical shrinkage increased with an increase in the prestretching ratio. DSC results of pretreated PAN fibers showed dependence not only on atmospheric conditions but also on the extent of prestretching.

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