Thermal-Shrinkage Investigation of the Chemical Reaction During the Stabilization of Polyacrylonitrile Fibers

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ABSTRACT: It has been proposed that during the stabilization of polyacrylonitrile fibers, the reaction is initiated in the amorphous region and then propagates to the ordered region. However, the evidence is unsatisfactory, and some is quite controversial. It has been confirmed in this study through an examination of the shrinkage behavior and properties of stabilized polyacrylonitrile fibers that the cyclization reaction is initiated at 160°C in the amorphous region and that it propagates to the ordered region at about 200°C. Most of the nitriles can be transferred to a ladder polymer structure when the stabilization temperature is beyond 240°C, and the key temperature during stabilization is 240°C. For a higher degree of cyclization, the stabilization temperature should not be below 240°C. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 3668–3672, 2009

Key words: amorphous; fibers; high temperature materials; infrared spectroscopy; thermal properties

INTRODUCTION

Of all the available precursors, polyacrylonitrile (PAN) fibers remain some of the best materials for making carbon fibers.[1–5] The thermal stabilization of PAN precursor fibers is considered to be a key step in the manufacture of carbon fibers, which involves the conversion of PAN into infusible, nonflammable fibers via heating at 180–300°C for 1 h or more in an oxygen-containing atmosphere. During the stabilization, the precursor fibers undergo various physical and chemical changes, such as the rearrangement of molecular chains, coloration and shrinkage, intramolecular or intermolecular cyclization and crosslinking, the diffusion and incorporation of oxygen, and the generation of volatile gases, which are influenced by the stabilization conditions and the properties of the precursor fibers.[6–9] Although extensive research has been conducted in this area, some important aspects pertaining to the stabilization of PAN fibers are not yet well understood.

Various theories abound regarding the initiation and propagation of stabilization reactions, but no definitive mechanisms have been proved.[10] It is generally thought that PAN is composed of laterally ordered domains and disordered (or amorphous) domains. The disordered regions, which consist of loops, folds, entangled chains, chain ends, defects, comonomer sequences, and tie chains, have a relatively loose structure and some free space. Therefore, it is easier for the C—C bond to rotate, for chain segments to move, and oxygen to diffuse.[11,12] Thus, some authors[11–13] have proposed that thermal stabilization reactions initiated in the amorphous part then propagate to the crystalline region. However, the evidence is not credible enough, and some is quite controversial.[14,15] In this study, we used thermal shrinkage for *in situ* measurements of the chemical stabilization reactions as they progressed. Through an examined of the shrinkage behavior and properties of stabilized PAN fibers, we further confirmed that the cyclization reaction initiates in the amorphous region and propagates to the ordered region at higher temperatures. Some new opinions are presented.

EXPERIMENTAL

Precursor

The selected PAN precursor was supplied by Huitong, Ltd. (Yangzhou, China) in tows of 3000 fibers with an average density of 1.18 g/cc and a mean diameter of 12.4 μm. This precursor fiber was most likely a copolymer of acrylonitrile and itaconic acid.
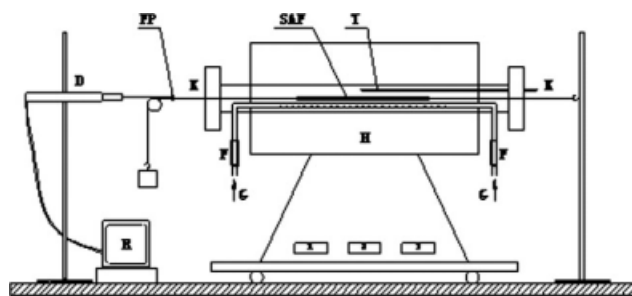
Figure 1 Apparatus used for shrinkage percentage measurements (CF = PAN fiber; D = displacement pickup; F = flow meter; FP = fixed point; G = purge gas; H = three-zone furnace; K = Kevlar; R = paperless record; T = thermocouple).

Stabilization

The stabilization was carried out in a batch-scale furnace. A fixed length of the precursor fiber was tied to Kevlar thread on both ends. For shrinkage monitoring during stabilization, the Kevlar thread was fixed at one end, and the other end was passed over a smooth pulley and connected to a weight; this corresponded to a tension of 0.0013 cN/dTex (Fig. 1). The movement of the weight was monitored with a displacement pickup and converted to shrinkage percentages. The results so obtained were called free shrinkage because the tension on the fibers was extremely low. The change in the Kevlar length was negligible in the studied range of temperatures. Output from the displacement pickup was amplified and noted by paperless recording every second. The stabilization was carried out in continuously flowing air (3 L/min). The temperature for the isothermal oxidation of the fibers was 100–280°C. The heating rate of the fibers was 2°C/min. The stabilized samples were labeled S-#-#, where the first number is the stabilization temperature (°C) and the second number is the stabilization time (h); for example, for sample S-240-24, the stabilization temperature was 240°C, and the stabilization time was 24 h.

Density

The density was measured at 25°C with the suspension method. Mixtures of toluene (density = 0.866 g/cc) and carbon tetrachloride (density = 1.585 g/cc) were employed for a fiber density in the 1.00–1.60 g/cc range. After the mixing, a solution containing a chopped-fiber sample was allowed to stand overnight. The solution was regulated with appropriate liquids until the fiber floated in the center of the solution. The density of the resulting solution was then determined with a density meter, and this density was extrapolated to be the density of the fiber specimen.

Infrared (IR) spectroscopy

IR spectroscopy was performed to observe the effects of the stabilization conditions. Fourier transform infrared (FTIR) measurements were made on a Nicolet (Madison, WI) Magna 550 FTIR spectrometer with a resolution of 2 cm^{-1} and 64 scans per sample. For a stabilized sample, an FTIR conversion index (A_I) could be defined in terms of the intensities of these peaks[16]:

$$A_I = I_O/(I_O + I_V) \tag{1}$$

where I_O is the measured intensity of the conjugated band at 1600 cm^{-1} associated with the developing structure and I_V is the measured intensity of the nitrile band at 2240 cm^{-1} belonging to the unmodified PAN molecule.

Tensile testing

Tensile testing was carried out with an Instron (Wenzhou, China) YD 001D tensile testing machine with a crosshead speed of 1 cm/min. In each case, at least 25 filaments with a gauge length of 2 cm were used for the tensile measurements, and their averages are reported here. Every sample was viewed at a magnification of ×1000 in a metallurgical microscope for the diameter measurements.

Other analyses

Changes in the color of the samples during stabilization were monitored by visual observation.

RESULTS AND DISCUSSION

Shrinkage during stabilization is considered to consist of two types: physical shrinkage and chemical shrinkage.[17] Figure 2 shows the shrinkage behavior of PAN fibers stabilized at different temperatures for 24 h. When the stabilization temperature is 180°C, constant shrinkage is not achieved. Therefore, the time was extended to 85 h, as shown in Figure 3. It is clear that the fiber does not undergo characteristic shrinkage until the temperature is greater than 160°C. Regular change is also seen, in that the amount of shrinkage increases with the stabilization time increasing, and then it levels off. With the stabilization temperature increasing, the shrinkage reaches stability more and more quickly, and this may be due to the fact that the reaction is accelerated at higher temperatures. In addition, the final amount of shrinkage also increases with the stabilization temperature increasing below 240°C. However, above 240°C, it is quite equal.

IR spectroscopy was performed on the as-received precursor and stabilized fibers, as shown in Figure 4.
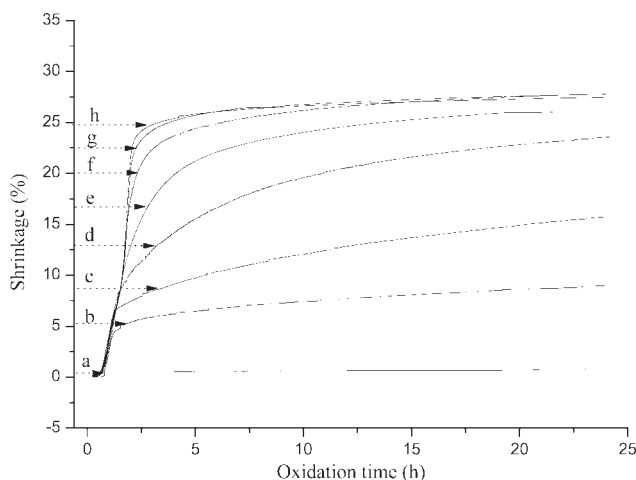
Figure 2 Shrinkage behavior during the stabilization of PAN fibers at different temperatures: (a) 100, (b) 160, (c) 180, (d) 200, (e) 220, (f) 240, (g) 260, and (h) 280°C.

Figure 4 IR spectra of PAN fibers: (a) precursor, (b) S-100-24, (c) S-160-24, (d) S-180-24, (e) S-180-54, (f) S-200-24, (g) S-220-24, (h) S-240-24, (i) S-260-24, and (j) S-280-24.

The peak at 2240 cm^{-1} is due to C≡N, and the peak at 1600 cm^{-1} is due to either the C=C group or the C=N group.[18] As can be seen from the spectra, with the stabilization temperature increasing, the peak at 2240 cm^{-1} decreases in intensity, whereas that due to the aromatized structure at 1600 cm^{-1} strengthens in intensity.

Table I presents values of A_I calculated according to eq. (1). With the stabilization temperature increasing, the value of A_I increases continually. When the stabilization temperature is above 240°C, the change is not obvious. This agrees with the change in shrinkage.

The effects of the stabilization time and temperature on the density of stabilized PAN fibers are shown in Table II. The density also increases with the stabilization temperature increasing. The density of the PAN fiber stabilized at 180°C for 85 h is still
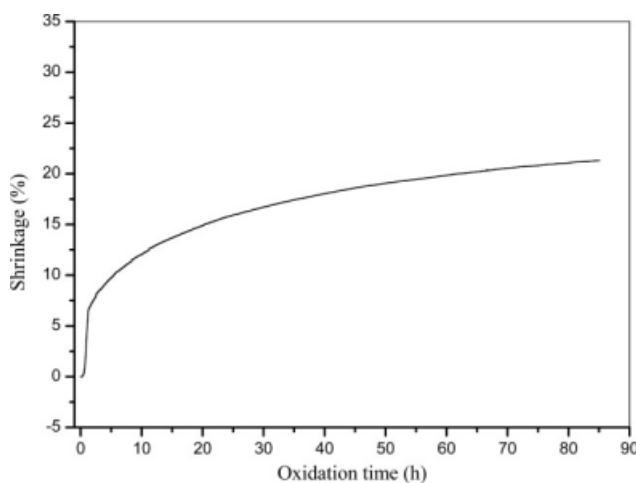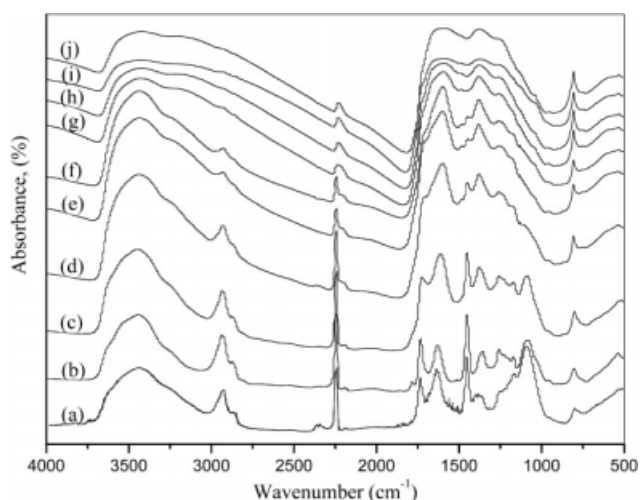
lower than that of the fiber stabilized at 200°C for 24 h. This agrees with the change in shrinkage. In addition, the densities of the PAN fiber stabilized above 240°C for 24 h are very close to the theoretical value of the completely aromatized structure (i.e., 1.6 g/cc).[19] This indicates that the degree of aromaticity above 240°C is very high.

The properties of the PAN precursor and fibers stabilized at different temperatures and for different times are tabulated in Table III. The difference between the precursor and S-100-24 is very small. However, the difference becomes obvious when the temperature is above 160°C.

As shown in Table III, the tensile strength of the stabilized PAN fibers decreases with the stabilization temperature increasing as a result of a loss of cohesive energy between the molecules.[20] The decrease is gradual below 160°C, then very sharp up to 200°C, and thereafter gradual again. The tensile strength of the PAN fiber stabilized at 180°C for 85 h is still lower than that of the fiber stabilized at 200°C for 24 h. If we take into consideration the aforementioned change in the shrinkage, density, and A_I, it seems that the effects of temperature and time are different. In other words, the effect of temperature cannot be replaced by the effect of time. From Table III, it is clear that the elongation to break starts to increase gradually, then rapidly accelerates to a maximum (S-180-24), and thereafter decreases sharply; above

Figure 3 Shrinkage behavior during the stabilization of PAN fibers at 180°C.

TABLE I
Measured A_I Values of the Stabilized PAN Fibers

Sample	S-160-24	S-180-24	S-180-85	S-200-24
A_I	0.3348	0.5809	0.6585	0.6607
Sample	S-220-24	S-240-24	S-260-24	S-280-24
A_I	0.7578	0.8098	0.7969	0.8077

TABLE II
Density of the PAN Precursor and Stabilized Fibers

Sample	Precursor	S-100-24	S-160-24	S-180-24	S-180-85
Density (g/cc)	1.1803	1.1790	1.1901	1.2511	1.2800
Sample	S-200-24	S-220-24	S-240-24	S-260-24	S-280-24
Density (g/cc)	1.3199	1.4129	1.5361	1.5770	1.5981

240°C, the decrease becomes very gradual. The increase in the elongation to break may be due to the shrinkage of the PAN fiber during stabilization. The decrease is due to the formation of a network structure at higher temperatures. The diameter also shows a peak at 180°C. The reason may be similar to the reason for the change in the elongation to break.

The color changes from white for the precursor to brown at 160°C and to black at 180°C; it remains black thereafter. The black color is believed to be due to the formation of a ladder ring structure.[21]

On the basis of the shrinkage behavior and properties of the stabilized PAN fiber, the conclusion to be drawn is that the chemical reaction mechanism is different at different temperatures.

It is generally thought that the molecular chains of PAN fibers have an irregular helical conformation because of the intramolecular dipolar repulsions of the nitrile groups. The cyclization of adjacent nitriles in a concerted manner to produce six-membered rings would require the helix to unwind, but this would be going in the direction of decreasing entropy and is contrary to the behavior of flexible-chain polymers with carbon backbones.[11] Energy is need for the rearrangement of the orientation of the molecular chains of PAN fibers. Therefore, temperature plays an important role in the stabilization process.

When PAN fibers are heated at 100°C, the properties of the stabilized fibers are similar to those of the precursor fibers, and this indicates that the PAN fibers do not undergo any physical or chemical reactions. The reason may be that both phases (amorphous and ordered) are rigid and the molecular chain is completely stable at this temperature.

At 160°C, the molecular chain of the amorphous phase becomes flexible and starts vibrating. The physical shrinkage, corresponding to entropic shrinkage, occurs because oriented amorphous polymeric chains revert to their random-coil configuration. Therefore, the increases in the elongation to break and diameter are obvious. Figure 3 shows that the peak at 1600 cm^{-1} increases a little, but the peak at 2240 cm^{-1} is still strong. In addition, the tensile strength decreases, the density increases, the value of A_I reaches 0.3348 (Tables I and II), and a brown color can be observed. All these observations indicate that the cyclization of nitrile groups occurs at this temperature. As the increases in the shrinkage and density are small, the extent is very low. The reason may be that the stabilization temperature is so low that most molecular chains do not have enough energy for cyclization.

At a higher temperature (ca. 180°C), the intermolecularly bound nitrile group pairs break, and the molecular mobility is enhanced. All the changes are great: the increases in the shrinkage, elongation to break, diameter, density, and A_I and the decrease in the tensile strength; this indicates that the nitrile units start cyclization to transfer to a ladder polymer structure in the disordered region of the PAN fiber because of the relatively loose structure of the disordered region and some free space. Therefore, the shrinkage achieves a stable value after about 80 h (Fig. 2), and this indicates that the reaction rate is quite slow. A black color can be observed at 180°C, and this is believed to be due to the formation of a ladder ring structure.

At an even higher temperature (ca. 200°C), the elongation to break and diameter begin to decrease obviously, and this indicates that the cyclization reaction has propagated to the order region because of the ordered region's relatively compact structure. The final amount of shrinkage increases a little in comparison with that at 180°C, and this may imply that the nitrile units start forming ladder polymer structures only at the boundary of the ordered region and not inside.

At 220°C, the tensile strength continues to decrease, and the elongation to break and diameter decrease rapidly. The density and A_I also increase

TABLE III
Properties of the PAN Precursor and Stabilized Fibers

Sample	Tensile strength (MPa)	Elongation to break (%)	Diameter (μm)
Precursor	482.87	18.25	12.56
S-100-24	475.93	18.43	12.61
S-160-24	434.76	20.64	12.84
S-180-24	271.73	24.92	12.94
S-180-85	200.91	14.1	13.03
S-200-24	186.71	10.95	12.98
S-220-24	167.75	6.37	12.75
S-240-24	154.83	1.98	12.15
S-260-24	143.21	1.69	11.94
S-280-24	133.76	1.6	11.18

sharply. All the results indicate that the ladder polymer is formed inside the ordered region.

When the temperature reaches 240°C, the shrinkage obviously increases and achieves a constant value quickly (27.4%). The elongation to break decreases from 6.37 (220°C) to 1.98%. The density of the stabilized PAN fiber is very close to the theoretical value of the completely aromatized structure, and the value of A_I reaches 0.7848. All these observations confirm that the fiber has enough energy to break the dipole interaction between molecular rods at this temperature, and most of the nitriles transfer to a ladder polymer structure. It seems that, for higher degree of cyclization, the stabilization temperature should be greater than 240°C.

Above this temperature, the value of shrinkage is quite equal, and this indicates that cyclization of the structure is completed at 240°C in 24 h. Because of the end of the cyclization reaction, the changes in the tensile strength, elongation to break, and A_I are not obvious. The changes in the density and diameter are due to other reactions (the oxygen reaction and dehydrogenation).

CONCLUSIONS

PAN fibers were stabilized at different temperatures until the shrinkage value was constant. The results indicate that the effects of temperature and time are different. In other words, the effect of temperature cannot be replaced by the effect of time. The reaction is initiated at 160°C and propagates to the ordered region at 200°C. Most of the nitriles can transfer to a ladder polymer structure at 240°C. The key temperature during stabilization is 240°C. For a higher degree of cyclization, the stabilization temperature should not be below 240°C.

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