

Preparation and Characterization of Carbon Fibers from Polyacrylonitrile Precursors

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ABSTRACT: The present work deals with the preparation of carbon fibers from polyacrylonitrile (PAN) fibers. The chemical composition and physical properties of the starting fibers were determined. The PAN fibers were stabilized in air at the temperatures (230, 270, and 300°C) with the heating time from 40 to 420 min. The effects of both final stabilization temperature and heating rate on the chemical and physical properties of the prepared stabilized fibers were studied. The chosen stabilized fibers samples were carbonized in argon atmosphere at the temperatures (1000, 1200, and 1400°C) with different heating rates 5, 10, 15, and 20°C min⁻¹. The effects of both carbonizing temperature and heating rate on the weight loss, density, elemental composition, and IR absorption spectra of carbonized fibers were also studied. The fiber sample,

which was carbonized at 1400°C, contains 97.55% carbon, 1.75% nitrogen, and 1.4% hydrogen. This means that carbonizing the stabilized fibers at 1400°C in argon atmosphere is suitable to get oxygen-free carbon fibers. Therefore, the used carbonizing temperature in the present work (1400°C) is suitable to produce moderate heat-treated carbon fibers with the heating rate of 15°C min⁻¹. The modulus of the prepared carbon fibers was compared to that of industrially produced fibers using the results of X-ray analysis. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 2074–2083, 2012

Key words: polyacrylonitrile fiber; carbon fibers; stabilization; carbonization; heating rates; chemical composition

INTRODUCTION

Currently, carbon fibers are predominantly made of polyacrylonitrile (PAN) precursors.^{1,2} PAN-based carbon fiber is stronger than other types³ because of its greater carbon yield (>50% of the original precursor mass).^{4,5} Furthermore, the wide availability of PAN precursor had triggered the production of carbon fiber. Most PAN-based carbon fibers are extensively applied in the composite technology.⁶ They are highly desirable for high performance composites of automotive and aerospace technologies due to their enhanced physical and mechanical characteristics.⁷ Liu et al.⁸ listed three steps for the conversion of PAN-fibers precursor to carbon fibers:

1. Stabilization or oxidation,
2. Carbonization (>1600°C).
3. Graphitization, that is, heating up to 3000°C.

The first step is essential and time consuming, where several chemical reactions occur such as cyclization, dehydrogenation, aromatization, oxidation,

and crosslinking, then ending with the formation of the conjugated ladder structure.^{9–11} Heat treatment involved in stabilization of PAN fibers is carried out usually at the temperature range of 200–300°C.^{12–15}

PAN fibers with optimum stabilization conditions can produce higher modulus carbon fibers. If the stabilization temperature is too high, the fibers can overheat and fuse or even burn. However, if the stabilization temperature is too low, the reactions will be slower, and the stabilization will be incomplete to yield carbon fibers of poor properties.

The carbonization step only occurs usually in nitrogen atmosphere. Some researchers proved that argon can also act as an inert gas in carbonization process.^{16,17} In such process, an aromatic growth takes place. The carbonization process may be carried out first via thermal pyrolysis up to 600°C with a low heating rate of (5°C/min) and the second stage with high heating rate. The optimum carbonization conditions are required to form a final carbon fiber with better properties.¹⁸ For further performance improvement, the carbonized fibers must undergo graphitization process at the temperature up to 3000°C. At this stage, about 99% of PAN fibers are converted into carbon structure. Carbon fibers of high modulus are produced in such conditions.^{19–22}

Unfortunately, in the literature, there is no exact temperature and time given to thermal conversion of

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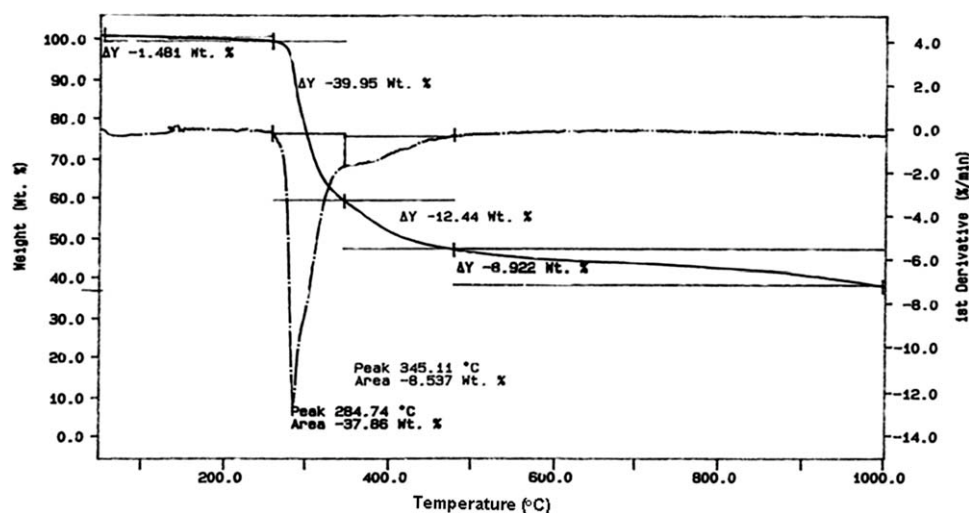


Figure 1 Thermogravimetric analysis (TGA) for PAN fibers.

PAN fibers to carbon fibers. Furthermore, there is no comprehensive study in the literature of the effect of temperature and time of both stabilization and carbonization steps on the conversion reactions. Therefore, the present work is undertaken to increase the understanding and give complete information of how the temperature and time of heating affect the thermal conversion of PAN fibers into carbon fibers. The changes in weight, shape, and density of PAN fibers under different preparation conditions were followed. Important information regarding the changes in the structure and phase formation is gained from the study of both infrared (IR) spectra and X-ray patterns of heat-treated PAN fibers. Furthermore, the chemical and phase composition of the prepared carbon fibers were compared to those of the industrially produced fibers.

EXPERIMENTAL

Materials

PAN fiber with the following specifications: tensile stress 360 g/tex, strain 28%, density 1.14 g/cm³, and melting point 250–325°C.

Experimental

1. Stabilization stage is an oxidation treatment for PAN fibers via heating at different temperatures (230, 270, and 300°C) in air to resist fusion during carbonization. These temperatures were achieved over different time periods (40 min up to 420 min).
2. Temperature in carbonization stage involving the heating of the preoxidized PAN precursor fibers varied from room temperature to 1400°C with different heating rates in argon gas atmosphere.

Methods of analysis

1. Elemental analysis was carried out using VARIO EL ELEMENTAL instrument to determine hydrogen, nitrogen, and carbon content of the prepared fibers and the blank samples.
2. X-ray diffraction (XRD) analysis was performed at room temperature using Philips XRD Apparatus type 1390, Cotarget, and Fe-filter ($\lambda = 1.542 \text{ \AA}$). The X-ray tube was operated at 30 kV and 20 mA. Samples were finely grounded and packed in aluminum holder. The diffraction angle 2θ was scanned at a rate of 1°/min.
3. IR analysis was performed on a Jasco/IR 300 E spectrophotometer.
4. Thermal gravimetric analysis (TGA), the PAN fiber sample was heated under nitrogen atmosphere in Differential Thermal Analyzer DTA7.
5. The microstructure of the prepared samples was studied by SEM Model Philips xL30.

RESULTS AND DISCUSSION

Characterization of the starting material

The starting material (PAN) was chemically and physically characterized. The results of chemical analysis indicated that it is a pure homopolymer and contains 67% carbon, 5% hydrogen, 27% nitrogen, and 1% oxygen. Figure 1 shows the TGA curve of PAN fibers. The weight loss value of the sample decreases in the temperature range of 230–300°C. It is clearly seen that the sample has lost about 62.79% of its original weight after heating at 1000°C.

The IR spectrum of PAN fibers is shown in Figure 2. It shows a peak at 3446 cm⁻¹ due to (C=NH), strong peak at 2939 cm⁻¹ due to (=CH₂), strong peak at 2243 cm⁻¹ due to (—C≡N), strong peak at 1740 cm⁻¹ due to

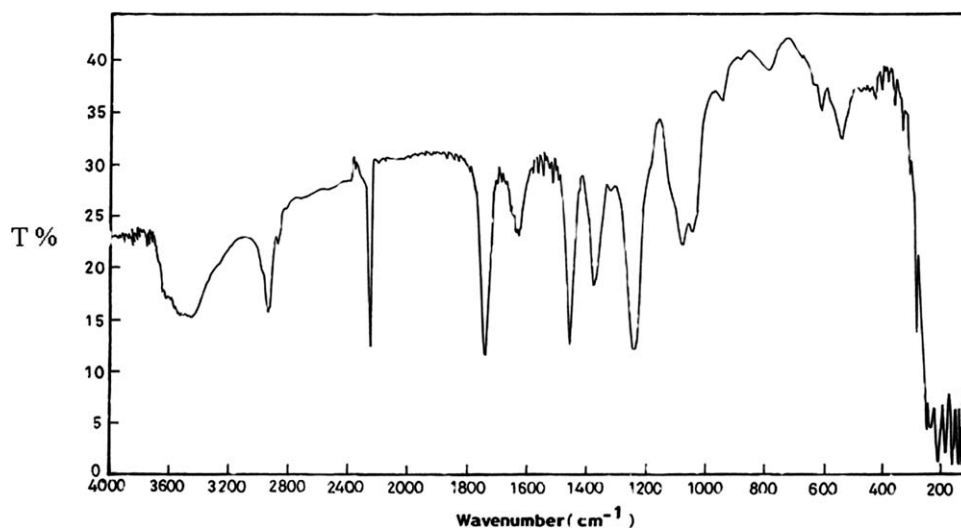


Figure 2 Infra red spectrum for PAN fibers.

the bending of ($\text{—C}\equiv\text{N}$), peak at 1455 cm^{-1} due to $\text{CHC}\equiv\text{N}$, peak at 1373 cm^{-1} due to (—C—C—), and peak at 1240 cm^{-1} due to (—C=C—).

Stabilization of PAN fibers

The PAN fibers were heated in air at temperatures: 230, 270, and 300°C at heating rates from 0.5 to 6°C min^{-1} up to the desired temperature. The effects of both final stabilizing temperature and treatment time on the chemical and physical properties of the stabilized fibers were studied.

Weight loss and shape of fibers

The weight loss in PAN fibers stabilized at different temperatures ($230\text{--}300^\circ\text{C}$) is determined and depicted in Figure 3. The main volatile by-products during the stabilization step of the PAN homopolymer in air are carbon dioxide (CO_2), water (H_2O), and hydrogen cyanide (HCN).²³ It is worthy to mention that the diffusion of oxygen and evolution of these gases in the form of CO_2 , H_2O , and HCN , have an effect on the volume of the fibers. This change in volume has to be avoided to conserve the preferred orientation obtained by pre-stretching the PAN fibers. Therefore, the change in the shape of the fibers was remarked under the influence of different stabilization process conditions, such as time of heating and temperature of oxidation. As shown in Figure 3, there is a considerable increase in the weight loss of the PAN fibers as the oxidation temperature increases from 230 to 300°C . The weight loss values can be arranged according to the oxidation temperatures as $230^\circ\text{C} < 270^\circ\text{C} < 300^\circ\text{C}$.

Figure 4 depicts the effect of the oxidation conditions (temperature and treatment time) on the shape of the fibers. One can see that as the temperature increases from 230 to 300°C and the treatment time

from 40 up to 420 min, the fibers preserve their shape (separate fibers) at 230°C ; in Figure 4(a), on the other hand, the fibers are fused and stuck together at 300°C ; while, in Figure 4(c), the fiber oxidized at 270°C occupied an intermediate position as shown in Figure 4(b). Therefore, heating the fibers at 230°C at slow rate (1°C min^{-1}) is more suitable for stabilizing the PAN fibers. Such conditions facilitate the escape of volatile byproducts like CO_2 , H_2O , and HCN from the bulk of the fibers without changing their shape.

Density and chemical composition of stabilized fibers

The relationship between the density of the PAN fibers and the treatment time is illustrated in Figure 5. As shown in Figure 5(a), the density of fibers increases as the stabilization temperature increases from 230 to 300°C . This appears clearly by heating

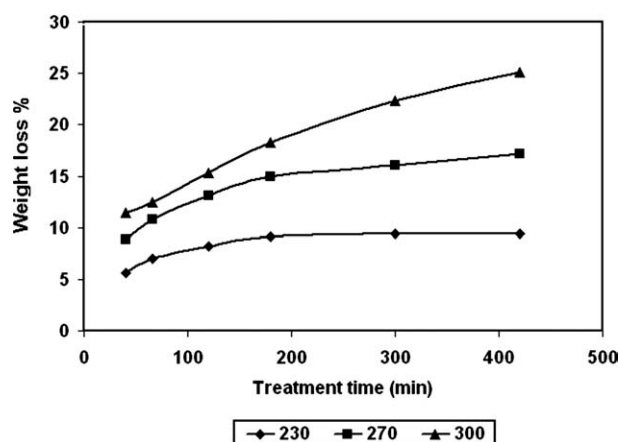


Figure 3 Effect of treatment time on weight loss of PAN fibers oxidized in air at $230\text{--}300^\circ\text{C}$.

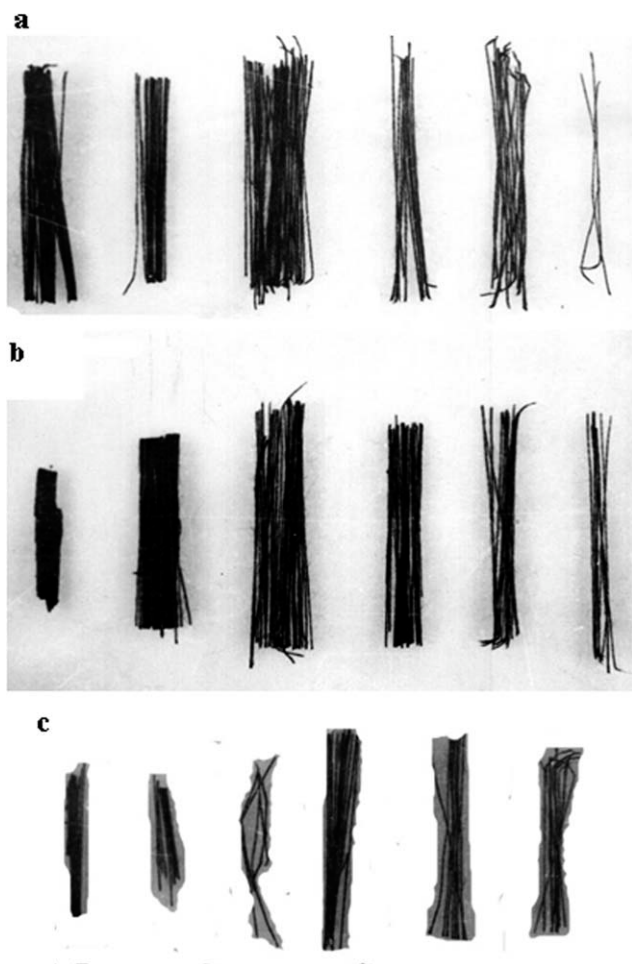


Figure 4 Effect of oxidation condition (temperature and heating time) on the shape of fibers at temperature: (a) 230, (b) 270, and (c) 300°C; heating time (40, 70, 120, 180, 300, and 420 min).

the fibers at relatively low rate. It is also shown that the density of the PAN fibers increases by decreasing the heating rate to a limited value. This value varies according to the temperature of stabilization. Heating rate of less than $1^{\circ}\text{C min}^{-1}$, practically, has no effect on the density of the PAN fibers stabilized at 230°C. The obtained results are in a good agreement with the change in weight loss of fibers at different treatment time as previously shown in Figure 3. This change in density of the fibers is mainly due to the reactions occurring in the PAN fibers with oxygen. Consequently, one can consider the density of the stabilized fiber is a measure of oxygen content. This is in good agreement with Fitzer et al.²⁴ who took the density value as an indication of the reaction rate during the stabilizing process.

The relationship between the hydrogen/carbon and nitrogen/carbon ratios of PAN fibers and the treatment time is shown in Figure 5(b,c). From these figures, it is observed that as the oxidation temperature increases from 230 to 300°C, the hydrogen/carbon ratio decreases, while the nitrogen/carbon ratio

increases. This appears more clearly as the oxidation temperature increases from 230 to 270°C. This means that the effect of temperature appears more strongly in this temperature range. There is a decrease in the hydrogen/carbon ratio and an increase in the nitrogen/carbon ratio values with decreasing the heating rate. Again, this appears slightly in the PAN fibers oxidized at 230°C and more pronouncedly as the oxidizing temperature was raised from 230 to 270°C. In general, as a result of oxidizing the PAN fibers in air atmosphere, the oxygen content of fibers increases at the expense of carbon, hydrogen, and nitrogen contents. Oxygen acts as a dehydrogenating agent and, in addition, forms oxygen-containing groups by a direct

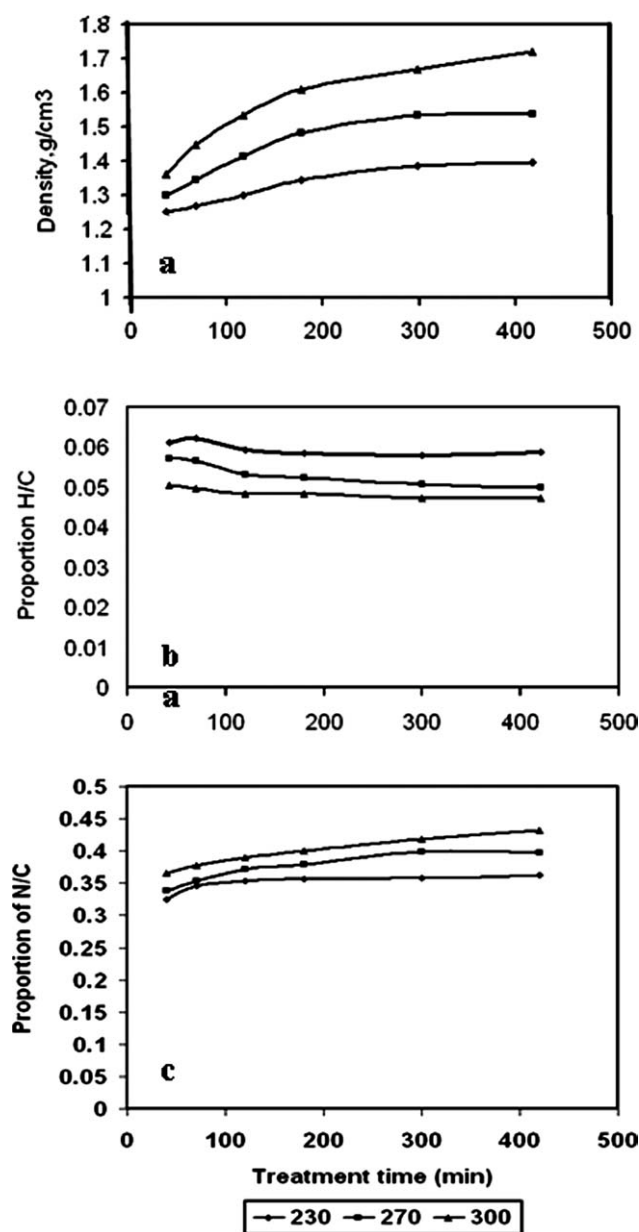


Figure 5 Effect of treatment time on (a) density, (b) the hydrogen/carbon ratios, (c) nitrogen/carbon ratios, of PAN fibers oxidized in air at 230–300°C.

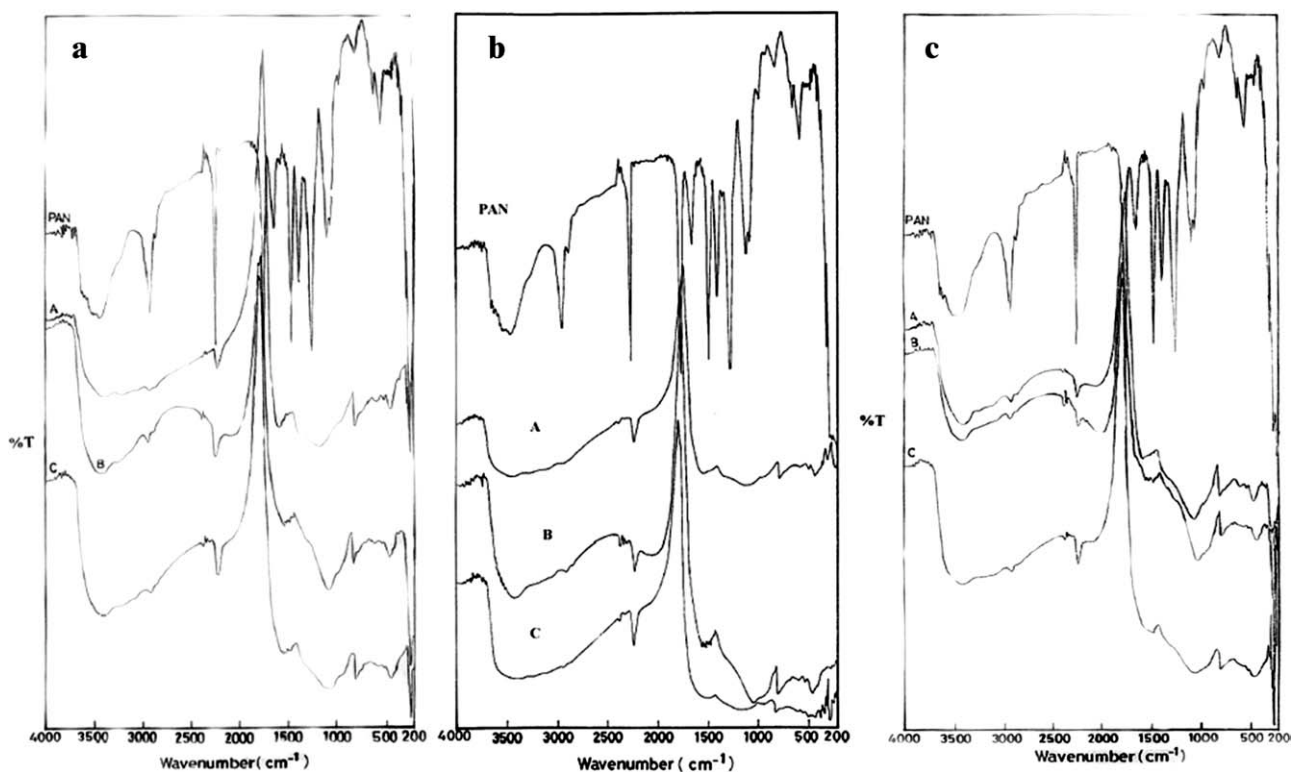


Figure 6 IR spectra for PAN fibers and the stabilized precursor at (a) 230° (b) 270°C and (c) 300°C with different heating time a) 70 min b) 180 min c) 420 min.

oxidation reaction.²⁵ Now, under the applied heating conditions the carbon content decreases faster than the nitrogen content and slower than the hydrogen content as clearly shown in Figure 5(b,c).

Infrared spectra of stabilized fibers

The infrared (IR) spectra of PAN precursor and the stabilized PAN fibers are shown in Figure 6(a–c). As seen from these figures, there is a notable decrease in the concentration of both ($-\text{C}\equiv\text{N}$) and ($=\text{CH}_2$) bands as a result of the stabilization process. The ($=\text{CH}_2$) band at 2943 cm^{-1} and the ($-\text{C}\equiv\text{N}$) band at 2239 cm^{-1} were used as indication of the dehydrogenation (oxidation) and cyclization reactions, respectively. This forms oxygen-containing groups such as $-\text{OH}$ band at 3400 cm^{-1} and ($-\text{C}=\text{O}$) in carboxyl at 1720 cm^{-1} . It was also found that the ($=\text{CH}_2$) concentration decreases simultaneously with ($-\text{C}\equiv\text{N}$) concentration. This means that the cyclization and dehydrogenation occur simultaneously.²⁶ The figures also show that the heating time up to temperature 300°C seems to have no effect on the IR spectra of stabilized fibers.

Carbonization of stabilized PAN fibers

The PAN fibers stabilized at 230°C with a heating rate of about 1°C min^{-1} were chosen to be carbonized into carbon fibers. The stabilized fibers were

heated in argon atmosphere with the heating rate of $5, 10, 15,$ and $20^\circ\text{C min}^{-1}$ up to the carbonizing temperature of 1400°C . The effects of carbonizing temperature $1000\text{--}1400^\circ\text{C}$ and also the heating rate $5\text{--}20^\circ\text{C min}^{-1}$ on the chemical composition of the carbonized fibers were studied. The changes in the phase composition as well as the microstructure of the carbonized fibers were followed by X-ray analysis and scanning electron microscope, respectively.

Effect of carbonizing temperature

Figure 7 shows the change in the carbon, nitrogen, and hydrogen contents of carbonized fibers with increasing the carbonizing temperature from 1000 to 1400°C . It is clearly seen that the carbon content has considerably increased with increasing temperature from 1200 to 1400°C . This increase in the carbon content is accompanied with a notable decrease in the nitrogen content. Less effect of carbonizing temperature on decreasing the hydrogen content is observed. On the other hand, the calculated oxygen content of the carbonized fibers considerably decreases with increasing temperature from 1200 to 1400°C , and its value reaches nearly zero in the fibers carbonized at 1400°C . This fiber sample contains 97.55% carbon, 1.75% nitrogen, and 1.4% hydrogen. This means that this temperature (1400°C) is high enough to get oxygen-free carbon fibers.

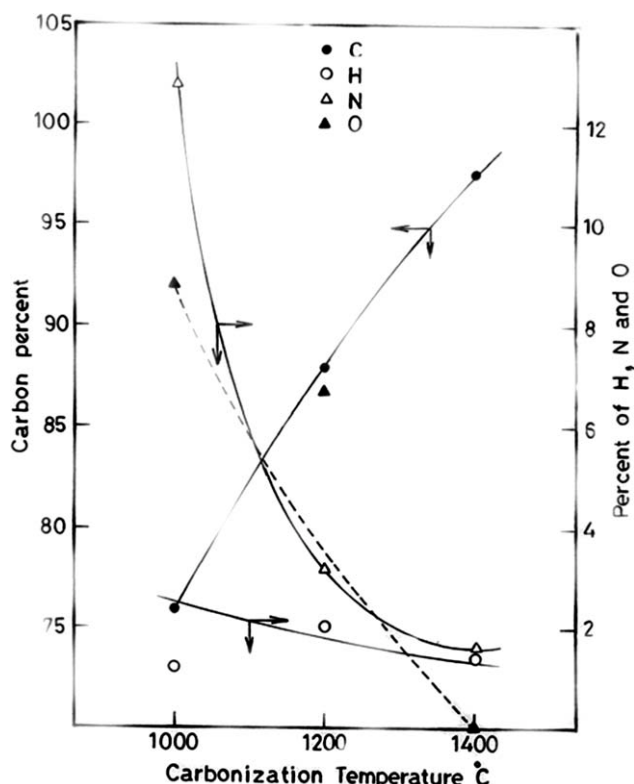


Figure 7 Effect of carbonizing temperature on chemical composition of carbonized fibers.

It is known that the tensile strength of the resulting carbon fibers does not directly increase by carbonizing the fibers at higher temperature.²² This means that a minimum strength occurs at heat treatment temperatures around 1600°C. This minimum strength is related to lattice defects caused by nitrogen loss. These defects are removed by further heating higher than 1800°C. This produces a more complete layer structure, and, consequently, the tensile strength of fibers increases again.²² Therefore, the used carbonizing temperature in the present work (1400°C) is high enough to produce moderate heat-treated carbon fibers at the heating rate of 15°C min⁻¹.

Density and chemical composition of carbonized fibers

The changes in the density and the chemical composition of carbonized fibers against the heating rate are depicted in Figure 8(a,b). It is clearly seen that the density of carbonized fiber increases considerably with the increase of the heating rates Figure 8(a). This is because of the removal of noncarbon elements as volatile materials during the carbonization process. Consequently, the density of the carbonized fibers can be used as an indication of reactions during this step of carbon fibers preparation.

The carbon, hydrogen, and nitrogen contents of the carbonized fibers are determined. The obtained

values are plotted against the heating rate as illustrated in Figure 8(b) from which it is clearly seen that as the heating rate increases from 5 to 20°C min⁻¹, the carbon content of the carbonized fibers increases. This increase takes place at the expense of hydrogen and nitrogen content. The fibers, which were carbonized at 1400°C with a heating rate of 15°C min⁻¹, contain more than 97% carbon, but they still contain about 3% of hydrogen and nitrogen. The changes in the chemical composition of carbonized fibers are due to the volatile by-products produced during the carbonization process. It is mentioned that the main by-product is formed during such process is HCN, in addition to water, ammonia, carbon oxide, and nitrogen. Elemental nitrogen is formed at the highest carbonization temperatures. The elemental analysis of the industrially produced carbon fibers showed that it still contains 2.54% hydrogen, beside carbon as the main constituent. Another important remark is that the calculated oxygen content decreases with the increase of heating rate, and its

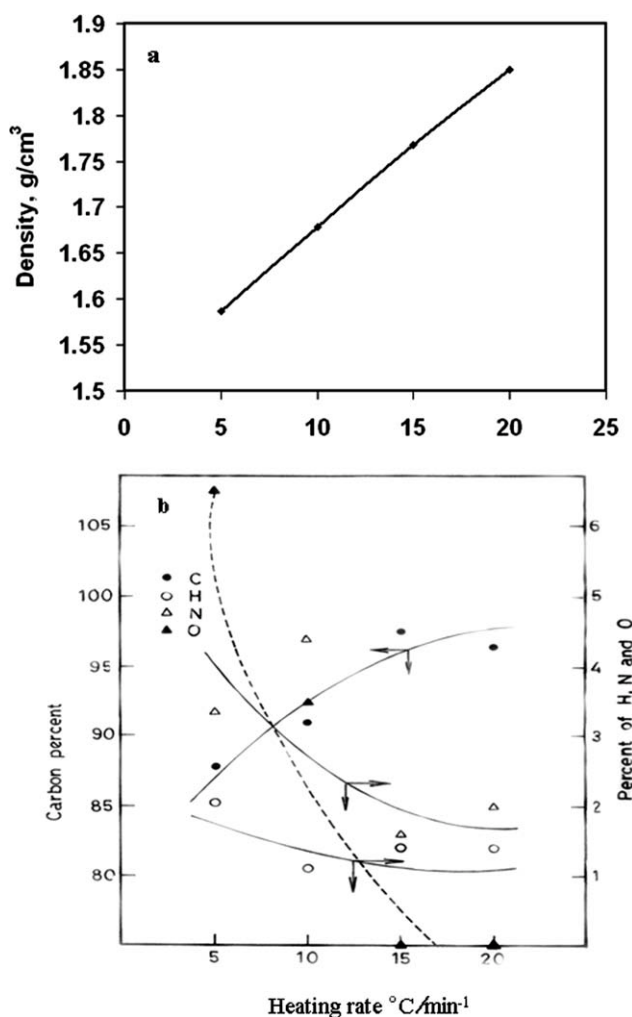


Figure 8 Effect of heating rate up to 1400°C on (a) density and (b) chemical composition of carbonized fibers.

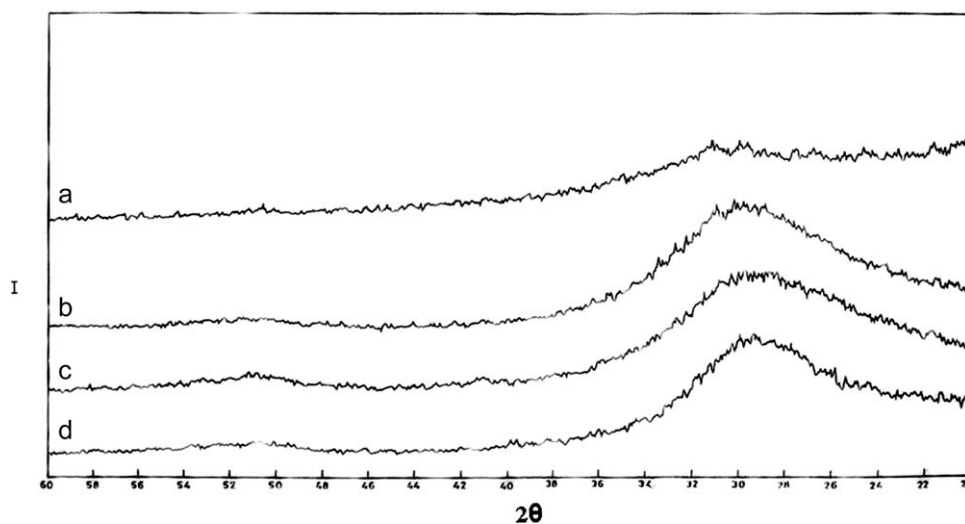


Figure 9 X-ray diffraction patterns of PAN fiber stabilized at 230°C (a) and then carbonized at 1000°C (b), 1200°C (c) and 1400°C (d).

value reaches nearly zero in the sample heated with a rate of 20°C min⁻¹.

Phase constitution of carbonized fibers

X-ray was chosen to follow the changes occurring in the phase constitution during the carbonization process of PAN fibers, which were first stabilized at 230°C. The X-ray patterns of the carbonized samples, besides the stabilized one as a starting material are illustrated in Figure (9). This figure shows the structure of the PAN fibers is destroyed during the stabilization process curve (a). Also, as the stabilized fibers are carbonized in argon atmosphere even at relatively low temperature (1000°C), the (002) reflec-

tion of carbon is observed on curve (b). By increasing the carbonizing temperature to 1200 and to 1400°C, there is an improvement in the shape of the fibers, curves c and d. This indicates that crystallite growth takes place despite the relatively low-firing temperature range (1000–1400°C). On the other hand, Figure 10 depicts the XRD patterns of industrially produced carbon fiber samples (one is a short fiber and the other is a continuous one). The XRD patterns of the two samples showed relatively high sharp (002) reflection. Moreover, the other (*hkl*) reflections appeared more clearly in the XRD pattern of the continuous carbon fiber sample. This indicates that the carbon layers are nearly aligned. This may be due to its carbonization at a relatively high

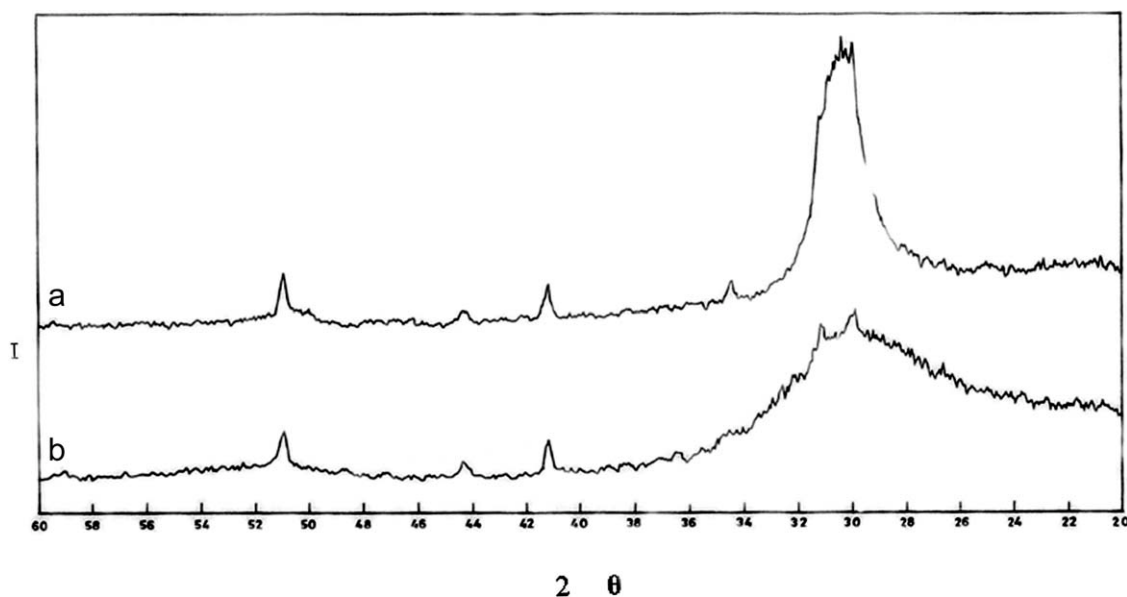


Figure 10 X-ray diffraction patterns of PAN fiber industrially produced C fibers: (a) continuous fiber and (b) short fiber.

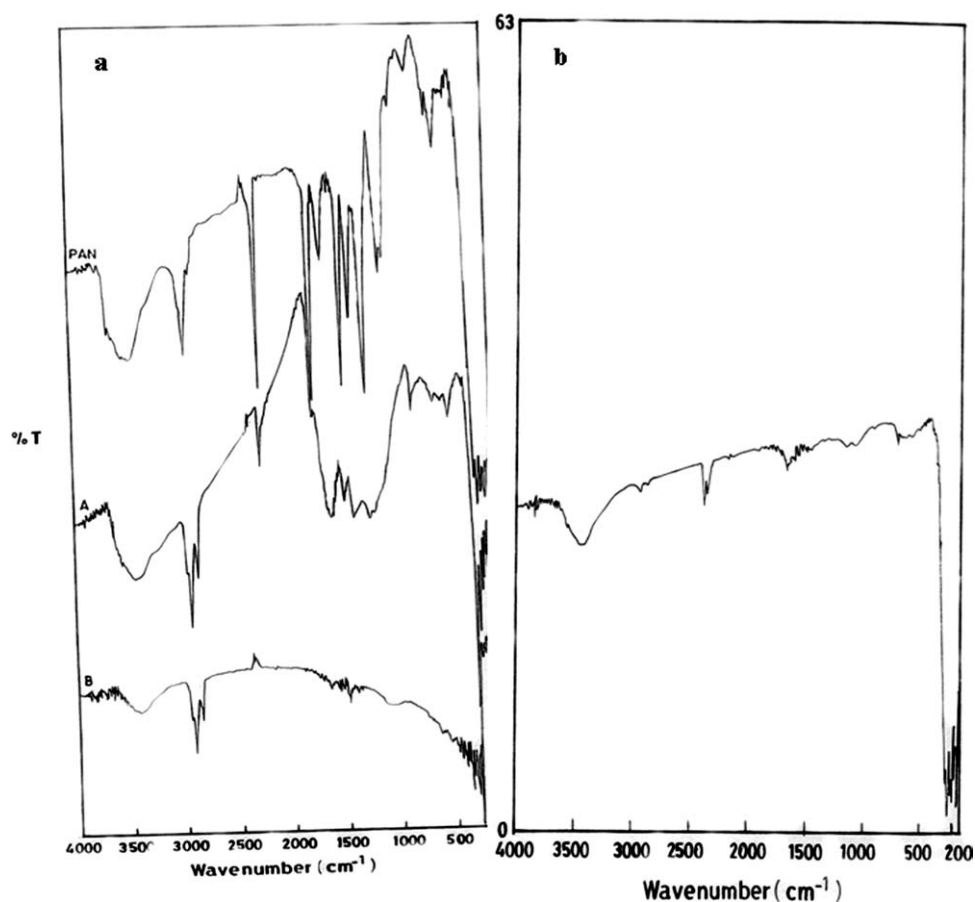


Figure 11 IR spectra for: (a) PAN fiber: (A) stabilized PAN fiber at 230°C and (B) carbonized at 1400°C and (b) graphite fiber.

temperature. The d -spacing determined from the (002) X-ray pattern reflection is nearly equal to 3.35 Å. This d -spacing value represents the distance between the carbon layers in the natural graphite.²⁶

The present X-ray results can be used for measuring the modulus values of the prepared carbon fibers. This method depends on using the X-ray reflection (002) arc as an indication of the preferred degree of orientation in carbon fiber. The half width of the bell-shaped intensity distribution of half-maximum intensity is taken as an indication of the relative degree of disorientation of the graphite layer from alignment with the fiber axis.²⁶ According to this method, the calculated values are 2.0°, 1.85°, and 1.6° for the carbon fiber samples prepared at 1000, 1200, and 1400°C, respectively. This means that the modulus values of the prepared carbon fibers increase as the carbonizing temperature increases from 1000 to 1400°C. On the other hand, the values of the industrially produced carbon fibers are 0.5° and 1.25° for continuous and short carbon fibers, respectively. They show higher modulus values compared to the prepared ones. This may be due to the relatively high temperature at which they were carbonized.

Infrared spectra

The infrared (IR) spectra of PAN fibers stabilized and carbonized PAN fibers as well as the commercial one are shown in Figure 11. As one can see from Figure 11(a), there is a gradual decrease in the IR bands of the starting material as the PAN fibers are stabilized in air at 230°C and then carbonized in argon at 1400°C. In the IR spectra of the carbonized sample, two weak bands only appeared at 2940 cm^{-1} and 2240 cm^{-1} due to the $=\text{CH}_2$ and $-\text{C}\equiv\text{N}$ bands, respectively. It is worthy to note that the spectra of industrially produced carbon fibers as shown in Figure 11(b) are almost identical to those of the prepared carbon fibers.

Microscopic study

The scanning electron micrographs (magnification $\times 350$) of stabilized PAN fibers and PAN carbonized fibers are shown in Figure 12. It is observed that the surfaces of carbonized fibers are smooth, and their diameter decreases with the increase of carbonizing temperatures. Diameter can be calculated for (a) stabilized PAN fiber is 17.58 μm , (b) carbonized PAN

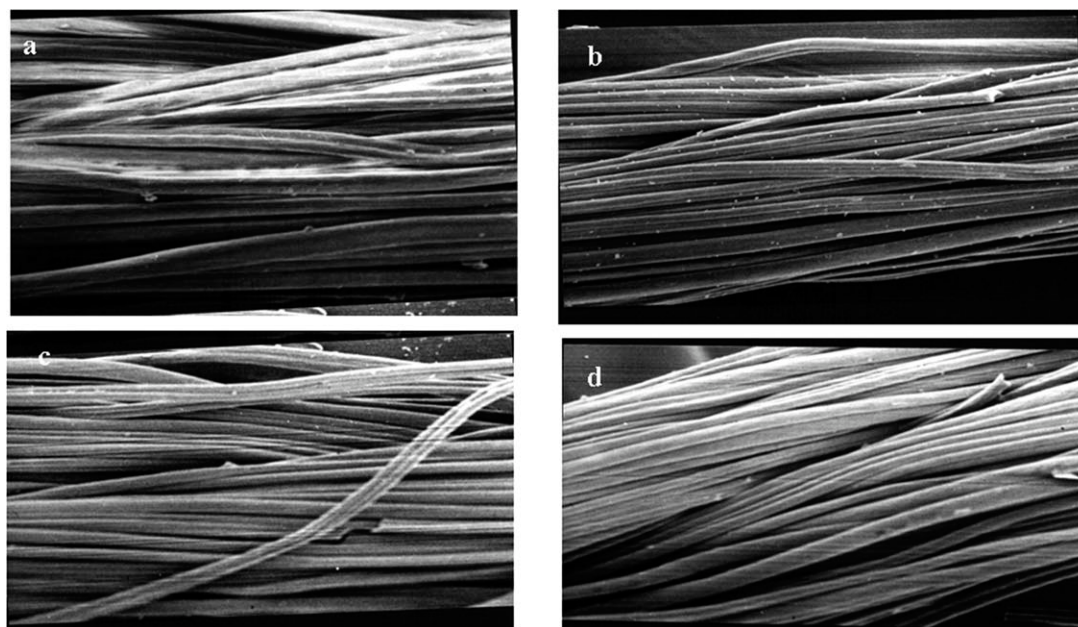


Figure 12 Scanning electron micrograph (X-350): (a) stabilized PAN fiber (230°C and 0.8°C min⁻¹), (b) carbonized PAN fiber (1000°C and 15°C min⁻¹), (c) carbonized PAN fiber (1200°C and 15°C min⁻¹), and (d) carbonized PAN fiber (1400°C and 15°C min⁻¹).

fiber at 1000°C is 9.95 μm, (c) carbonized PAN fiber at 1200°C is 9.4 μm, and (d) carbonized PAN fiber at 1400°C is 7.5 μm.

CONCLUSIONS

- Both weight loss and density of fibers increased as the stabilized temperature is increased from 230 to 300°C. This is a result of a relatively high rate of diffusion of oxygen and evolution of by-products. The stabilized fibers preserve their original shape as the stabilization heating rate is less than 1°C min⁻¹ and are badly shaped and stick to each other, when oxidized at a higher rate.
- The carbon content in the stabilized fibers increases as the carbonizing temperature and heating rate increases. This is accompanied with a decrease in the nitrogen and hydrogen contents. This change in the composition is due to the evolution of volatile by-products such as HCN, H₂O, NH₃, and CO₂.
- The oxygen content decreases considerably with increasing the carbonizing temperature and heating rate, and its value is nearly zero in the fibers carbonized at 1400°C with a heating rate of 15°C min⁻¹. These conditions are suitable to produce carbon fibers containing about 97% carbon.
- X-ray analysis depicted that the structure of stabilized fibers is destroyed; on the other hand, the (002) reflection of the carbon was detected in the sample carbonized at 1000°C. Its shape is improved with increasing tempera-

ture to 1400°C. The diameter of fibers is decreased from 9.95 μm to 7.5 μm with the increase of carbonizing temperature from 1000 to 1400°C, respectively.

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