

STRUCTURAL CHARACTERIZATION OF THERMALLY STABILIZED POLY(ACRYLONITRILE) FIBERS BY MEANS OF X-RAY DIFFRACTION, FT-IR SPECTROSCOPY, AND TGA ANALYSIS**Tuba DEMIREL**

Department of Mechanical Engineering, Erciyes University, Kayseri, Turkey

ORCID NO: 0000-0002-5760-3705

Md. Mahbubor Rahman

Department of Textile Engineering, Bangladesh University of Textiles, Tejgaon, Dhaka, Bangladesh

ORCID NO: 0000-0001-7104-9459

Prof. Dr. Ismail KARACAN

Department of Textile Engineering, Erciyes University, Kayseri, Turkey

ORCID NO: 0000-0002-9047-1011

ABSTRACT

The structure and effects of thermally stabilized PAN original fibers were characterized utilizing a mixture of volume density, color change observations, flame tests, X-ray diffraction (XRD), infrared spectroscopy (FT-IR), and thermogravimetric analysis (TGA) measurements. The results obtained from the analysis of XRD work showed the conversion of the original molecular structure from a highly laterally ordered condition to a disordered amorphous structure. The experimental results acquired from FT-IR analysis indicated rapid and concurrent aromatization and dehydrogenation reactions assisted by the formation of oxygen-containing functional groups. TGA analysis showed a carbon yield of 72% at 1000 °C. The application and use of NH₄Br pretreatment are expected to increase the productivity of carbon fiber processing at lowered cost by significantly reducing the processing time necessary for the successful completion of thermal stabilization reactions.

Keywords: Stabilized PAN Fibers, Thermal Stabilization, Ammonium Bromide (NH₄Br) salts, XRD, FT-IR, TGA.

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ÖZET

Termal olarak stabilize edilmiş orjinal PAN liflerinin yapısı ve etkileri, hacim yoğunluğu, renk değişimi gözlemleri, alev testleri, X-ışını kırınımı (XRD), kızılötesi spektroskopisi (FT-IR) ve termogravimetrik analiz (TGA) ölçümleri kullanılarak karakterize edilmiştir. XRD çalışmasının analizinden elde edilen sonuçlar, orijinal moleküler yapının yanal olarak düzenli bir durumdan tamamen düzensiz bir amorf yapıya dönüşümünü göstermiştir. FT-IR analizinden elde edilen deneysel sonuçlar, oksijen içeren fonksiyonel grupların oluşumunun yardımcı olduğu hızlı ve eş zamanlı aromatisasyon ve dehidrojenasyon reaksiyonlarını göstermiştir. TGA analizi, 1000 °C'de % 72'lik bir karbon verimi göstermiştir. NH₄Br ön işleminin uygulanması ve kullanımının, termal stabilizasyon reaksiyonlarının başarılı bir şekilde tamamlanması için gerekli işlem süresini önemli ölçüde azaltarak düşürülmüş bir maliyetle karbon liflerinin üretkenliğini arttırması beklenmektedir.

Anahtar Kelimeler: Stabilize olmuş PAN lifler, Termal Stabilizasyon, Amonyum Bromür (NH₄Br) tuzları, XRD, FT-IR, TGA.

1. INTRODUCTION

Carbon fibers are used as reinforcing elements in polymer, metal, and ceramic matrices (Farsani, 2012). Carbon fibers are widely used because of their low weight, low density, and high chemical resistance (Zhang et al., 2020). Carbon fiber composites have a strength to weight ratio 5 times that of American Iron and Steel Institute (AISI) 1020 steel and possess superior fatigue behavior to any metal (Sha et al., 2019). More than 90% of carbon fiber producers in the world widely use original PAN (also known as Polyacrylonitrile or acrylic) fiber (Dang et al., 2020; Haoa et al., 2018; Bhatt and Goeli, 2017). Comonomers are required for carbon fiber formation of original PAN fibers (Farsani, 2012; Farsani et al., 2006).

The PAN fiber is heated above 180–200 °C where an autocatalytic reaction of cyclization takes place through a free radical mechanism. The stabilization stage involves heating the PAN fiber in an oxygen atmosphere through a temperature range of 200-300 °C, during which oxygen binds to the fiber, thus ensuring that the fiber can withstand high temperatures during the carbonization phase (Dang et al., 2020; Ge et al., 2019; Sun et al., 2009). Throughout stabilization, the original PAN fiber converts to a golden blonde color, followed by a deep brown color, and finally a dark black color (Wei et al., 2019). In the thermal stabilization step, dehydrogenation, cyclization, and oxidation reactions lead to the structural formation and then the carbonization stage includes inter cross-linking bond reactions (Karacan and Meseli, 2018, Dalton et al., 1999). Chemical methods include solutions of inorganic-organic acids, Lewis acids, bases, oxidizing compounds, and transition metal compounds. Ionic liquids are ideal for easy absorption of original fibers. Ionic liquids provide high thermal stability by providing catalysts for many chemical reactions (Maghe et., 2016). At the same time, the aqueous solution of NH₄Br is an ionic liquid (Zhao and Guoxin, 2013). Halogens are added as flame retardants, which in order of decreasing effect are I, Br, Cl, and F elements, respectively (Visakh and Arao, 2015).

The aim of this study, therefore, is to examine the pre-effect of PANfibers thermal stabilization reactions using NH₄Br. Ammonium salts were shown to accelerate thermal stabilization before the carbonization step. Structural changes occurred at the molecular level of the PAN thread during the thermal stabilization phase. At a molecular level, the structural changes that occur during thermal stabilization of PAN fibers were carried out using a combination of TGA, FT-IR, and XRD analysis measurements. The effects of these changes were quantified by measuring the density of stabilized PAN fibers.

2. MATERIAL AND METHODS

2.1. Determination of experimental parameters

The most important parameters in the thermal stabilization method; It has been determined that the waiting time in the heat treatment, the stabilization temperature, the heat treatment in the air environment, and the heating rate. As a result, in this exploratory, it was purposed to shorten the cyclization time of the fibers by applying chemical pretreatment with NH₄Br aqueous solution before the stabilization stage of the PAN fiber in addition to the basic parameters. It is also thought that energy consumption costs in the stabilization process will be reduced by chemical pretreatment. Determination of Experimental Parameters as shown in Table 1.

Table 1. Parameters using on experiments and annealing stages of PAN fibers NH₄Br impregnated chemical solution.

Parameters		Stabilization temperature from 200 to 250 °C					
		200	210	220	230	240	250
Stabilization in air		✓	✓	✓	✓	✓	✓
Stabilization time (min)	Exp 1.	5	5	5	5	5	5
	Exp 2.	15	15	15	15	15	15
	Exp 3.	30	30	30	30	30	30
	Exp 4.	45	45	45	45	45	45
	Exp 5.	60	60	60	60	60	60
	Exp 6.	75	75	75	75	75	75
Heating rate in each temperature step (°C/min)		2	2	2	2	2	2
Ammonium bromide (NH ₄ Br) impregnated pretreatment		✓	✓	✓	✓	✓	✓

2.2. Materials

The commercially produced PAN copolymer used in the present investigation incorporates composition was 90% acrylonitrile (AN) and 10% vinyl acetate (VA) monomers. These PAN original fibers are a linear density of 59.7

± 0.1 Tex per 180 filaments together with a thickness of $22 \pm 0.2 \mu\text{m}$. NH_4Br decomposes in aqueous solutions by applying heat through occurring two independent chemical reactions given in the formula (1) and (2).



Chemical pretreatment with flame retardant 5% NH_4Br aqueous halogen solution at 90°C temperature was immersed for 1 hour. This flowchart of the experimental process was shown in Fig. 1.

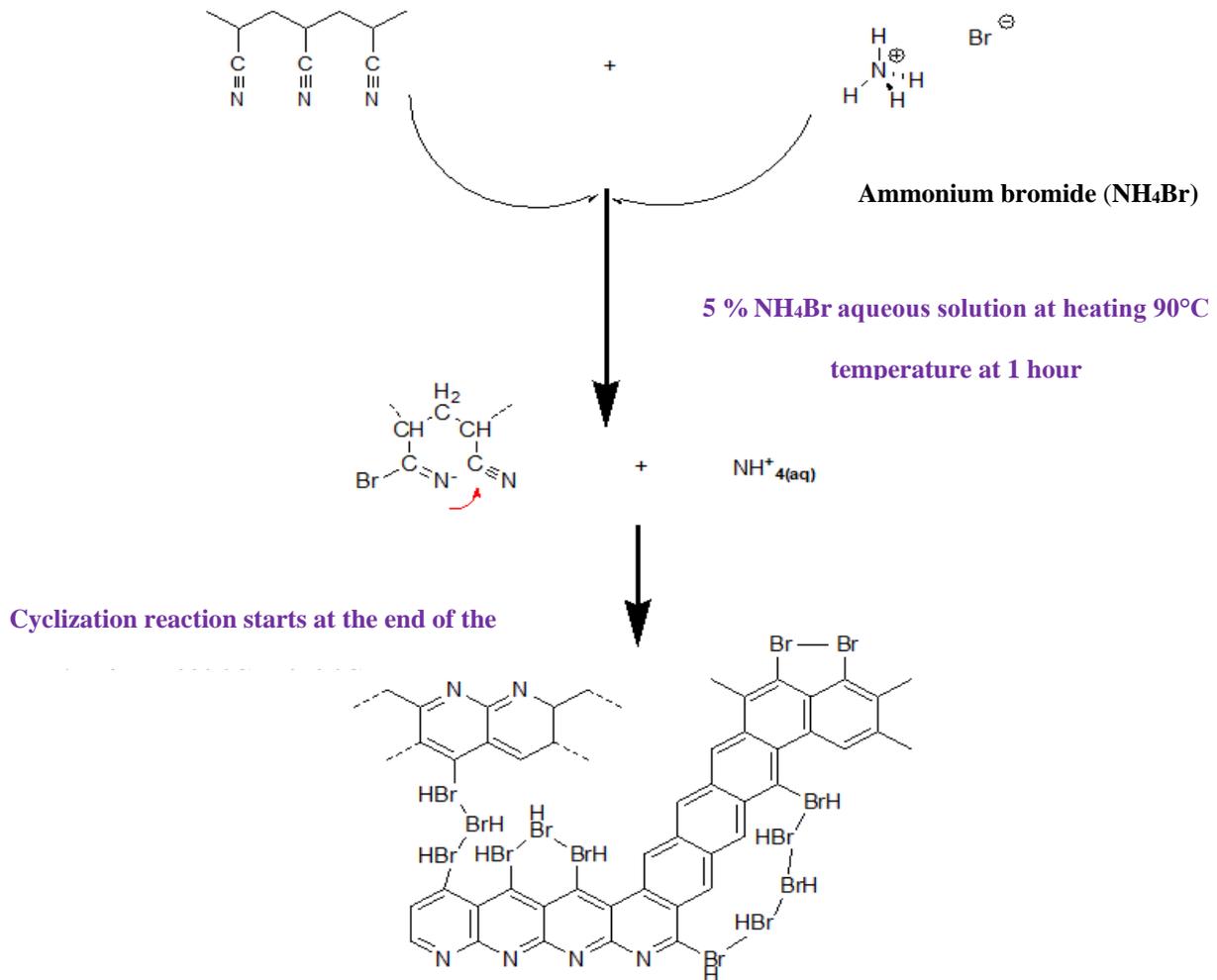


Fig. 1. The agent NH_4Br halogen salt in the stabilization stage in the PAN polymer.

For NH_4Br solution impregnation, we wrapped the samples in stainless steel frames. Prior to pretreatment, original PAN fibers were washed in 10% aqueous ethanol solution for 1 hour to eliminate impurities from the surface followed by washing under flowing water for 1 hour. As a final step, the samples were allowed to dry overnight. 5% (w/w) NH_4Br aqueous solution was used to impregnate PAN fibers: the pH value of the solution was measured as 5.82 at 25°C . Thermal stabilization of PAN fiber was carried out in air at a room temperature of 10°C from 200 to 250°C with stabilization times of 5 min, 15 min, 30 min, 45 min, 60 min, and 75 min, separately. A heating rate of $2^\circ\text{C}/\text{min}$ was utilized to 200- 250°C followed by a cooling rate of $2^\circ\text{C}/\text{min}$. The temperature rose from 10°C to 200- 250°C then decrease by slowly cooling to 10°C .

2.3. Fiber stabilization

Thermal stabilization process was performed using NH₄Br impregnation PAN multifilament fibers via multi-step annealing approach at 250 °C for different treatment time ranging from 5 to 75 minutes. Thermal stabilization of PAN fibers was performed in an air atmosphere (Fig. 2). The multi-step approach as following:

1. Heating from 10 to 200 °C at 2 °C /min holding for a given stabilization time.
2. From 200 to 210 °C at 2 °C/min.
3. From 210 to 220 °C at 2 °C/min.
4. From 220 to 230 °C at 2 °C/min.
5. From 230 to 240 °C at 2 °C/min.
6. From 240 to 250 °C at 2 °C/min.
7. Cooling from 250 °C to room temperature at 2 °C/min.

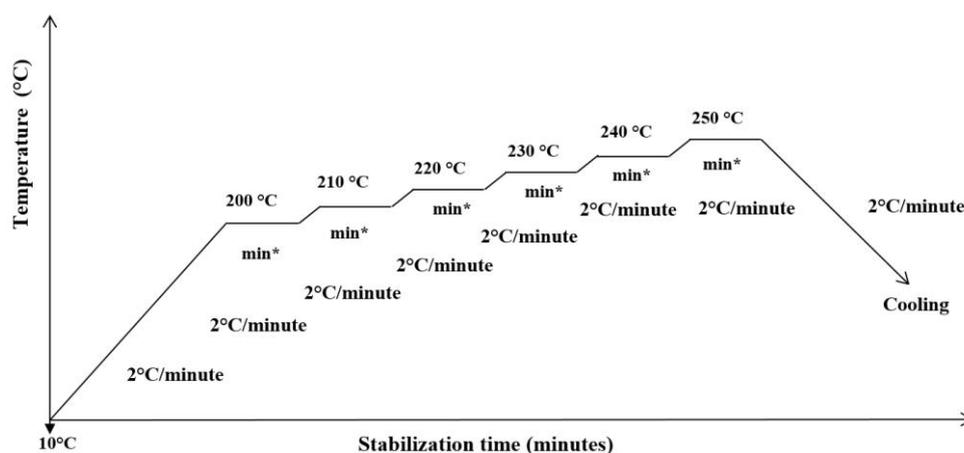


Fig. 2. Annealing stages of PAN filament impregnated chemical solution.

3. RESULTS AND DISCUSSION

During thermal stabilization, atmospheric oxygen accelerates cyclization and oxidation reactions. In the present investigation, the effect of NH₄Br impregnation of PAN fiber was investigated in detail. The burning (non-flammability) test is a suitable pretesting method to determine textile fiber categories. Stabilized PAN fibers were directly exposed to a match flame to determine its burning rate and properties.

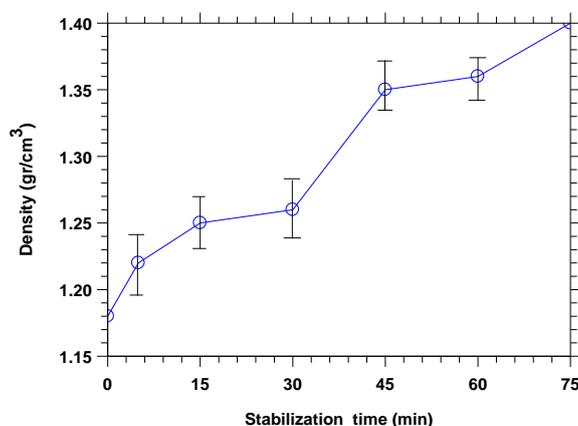


Fig. 3. Change of volume density as stabilized PAN fiber in stabilization time on-air atmosphere.

The volume density of the original PAN fiber is 1.18 gr/cm³. The density values increase from 1.18 to 1.40 gr/cm³ in Fig. 3 because of ongoing cyclization and oxidation reactions. The density values of carbonized fibers decrease with enhancing density values of the stabilized PAN samples. It seems that high-density values of stabilized samples result in fibers with low tensile strength values due to the formation of micropores. Increasing the amount of oxygen in the atmosphere has increased the density of the fiber. Volume density of fiber shows that it is an effective approach for the evaluation of the physical properties of the stabilized PAN fiber.

3.1. Evaluation of fiber characterization

3.1.1. X-ray diffraction (XRD) analysis

XRD profiles were acquired employing nickel filtered CuK α radiation ($\lambda=0.154$ nm). The Bruker[®] AXS D8 X-ray diffractometer is used for XRD work using voltage and current adjustments of 40 kV and 40 mA, respectively. The thermal stabilization process seems to have a great influence on crystalline structure in terms of crystal dimension and degree of crystallization for the laterally ordered structure. Observation of gradually lost laterally ordered structure was made with progressing stabilization activities. Detailed analysis of fitted XRD traces of original and stabilized PAN fibers in the 5% NH₄Br solution are presented in Fig. 4 (A) and (B). The results indicate that the X-ray stabilization index enhanced very rapidly following the rising stabilization time in Fig. 4. (B). In the present work, X-ray stabilization index data were observed to rise with rising stabilization time in Fig. 4. The results presented in Fig. 4 indicate that the amounts of apparent X-ray crystallinity exhibited a decreasing trend and an increasing trend was observed in the case of amorphous fraction values. The values of X-ray crystallinity indicated a decreasing tendency starting from 19% to 5%. However, the values of the amorphous fraction exhibited a reverse tendency, increasing from 81 to 95% with increasing stabilization time. XRD curves of original and stabilized PAN fibers for stabilization times are given in Fig. 4(A).

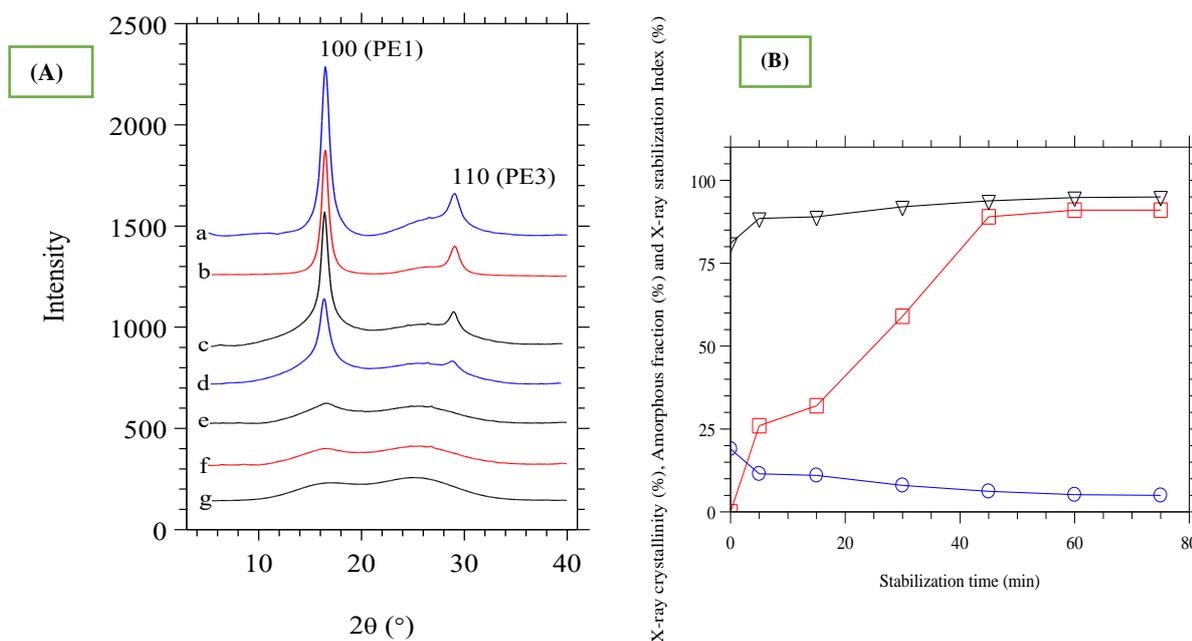


Fig. 4. (A) XRD curves of original (a), and stabilized PAN fibers impregnated in 5% NH₄Br as a function of stabilization times (in each stage) (b) 5 min, (c) 15 min; (d) 30 min; (e) 45 min; (f) 60 min; (g) 75 min. (B) X-ray order, amorphous ratio and X-ray stabilization Index values as a function of stabilization time. (□) X-ray stabilization Index (%), (O) X-ray crystallinity (%), and (∇) Amorphous ratio (%).

3.1.2. Thermogravimetric (TGA) analysis

A Perkin Elmer diamond TGA system was used to obtain thermograms of the original and heat stabilized samples. Throughout the TGA experiments, the maximum temperature was 1000 °C. The heating speed was 10 °C/min. A

continuous flow of nitrogen gas (200 ml/min) was kept during the experiments. Weight calibration was performed using 20 mg standard weight at 20 °C in both systems.

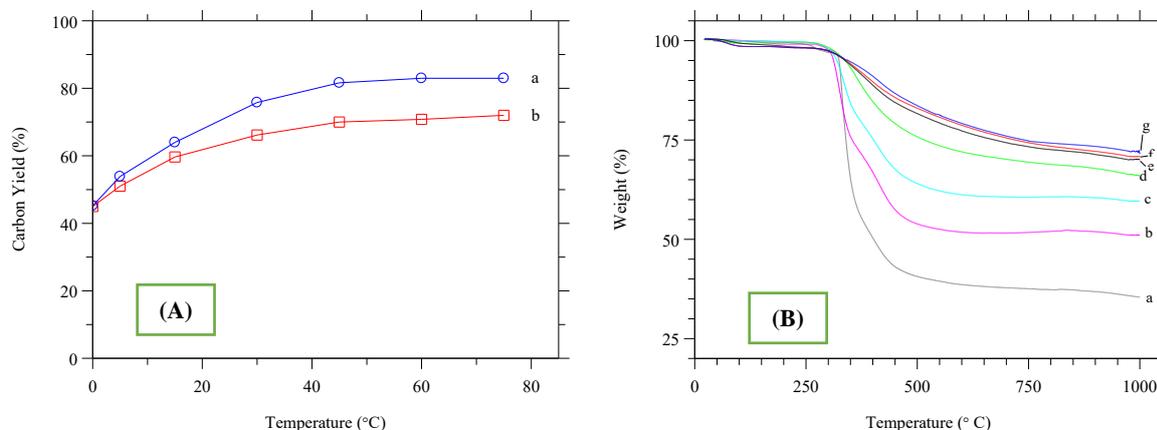


Fig. 5. (A) Comparison of carbon yields of original and stabilized PAN fibers impregnated in 5% NH_4Br solution, and stabilized at 250 °C by a multistep annealing approach for different stabilization period, at different temperatures (a) 500 °C (O) and (b) 1000 °C (□) **(B)** TGA thermograms of original and stabilized PAN multifilament impregnated with 5% NH_4Br and stabilized at 250 °C by multi-step annealing approach for different stabilization times (in each stage) (a) original PAN (b) 5 min (c) 15 min (d) 30 min (e) 45 min (f) 60 min (g) 75 min.

Total mass loss at 1000 °C for the original PAN fiber is 55% together with the carbon efficiency of 45%. TGA thermograms of NH_4Br impregnated and stabilized PAN samples exhibit rising thermal stability and carbon yield due to the impact of the enhancing intermolecular. TGA thermograms presented in Fig. 5 (A) show an increase in carbon yield with the increase of stabilization time, which indicates a decrease in mass loss caused by the progressing aromatization process. Owing to the formation of a highly cross-linked and aromatized structure, thermally stabilized PAN loses mass above a broader temperature interval although the original PAN loses weight above a narrow temperature interval. A severe thermal decomposition is observed for thermally stabilized PAN fibers with a stabilization time of 5 min at temperatures between 300 and 450 °C with a weight loss of 63.5% at 500 °C and 56.6% at 1000 °C. With the increase of stabilization time, the weight loss decreases gradually in between 50 °C and 450 °C in Fig. 5 (B). For the 75 min stabilization time, thermally stabilized PAN fibers, weight loss becomes 17% at 500 °C and 28% at 1000 °C. A comparison of the carbon efficiency for the original and NH_4Br impregnated and stabilized PAN fibers at temperatures of 500 °C and 1000 °C is presented in Fig. 5 (A). Analysis of the TGA thermograms shows that due to the formation of oxidation-based crosslinking and aromatization reactions the thermally stabilized PAN obtain higher thermal stability. The results obtained here illustrate that the carbon yield value increases with the raise of stabilization time. The carbon yield value for the 5 min stabilized PAN sample was 54% and 51% at 500 °C and 1000 °C, respectively. In the present experimental work, NH_4Br impregnated 75 min stabilized PAN sample presents a maximum carbon yield value of 83% at 500 °C and 72% at 1000 °C. A gradual increase of carbon yields is observed at 500 and 1000 °C for different stabilization times from 5 min to 75 min in Fig. 5 (A).

3.1.3. Infra-red spectroscopy (FT-IR) analysis

A Perkin Elmer® Spectrum 400 FT-IR spectrometer was used during the present investigation. For all the samples, 50 interferograms were collected and averaged. All the averaged interferograms were converted by using medium the Norton-Beer apodization function. Fiber images were performed using a 40X magnification with an optical microscope (Nikon ME 600L).

The results of non-flammability tests are presented in Fig. 6. Modification of colors confirms the existence of a thermally stabilized structure of the PAN filament. It has been observed that the fiber burning is influenced by the accelerated cyclization reactions and results in the non-burning behavior after a stabilization time of 30 min according to other 5 min and 15 min stabilization times (min). The mass loss that occurs throughout thermal stabilization reactions causes a decrease in fiber thickness. The stabilized PAN fiber thickness was reduced from

22 to 14 μm for a stabilization time of 75 min. The fiber thickness diminished with raising stabilization time because of mass losses occurring during thermal stabilization reactions.

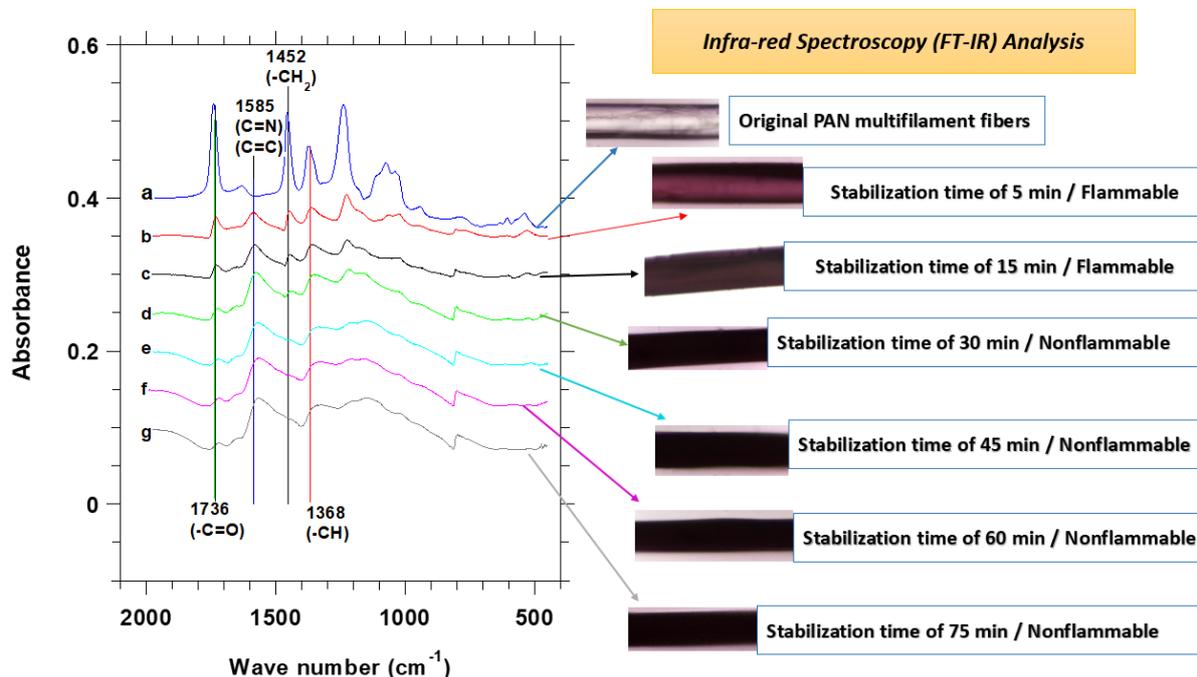


Fig. 6. Infrared spectra in the 2000–450 cm^{-1} region of original (a), and thermally stabilized PAN impregnated in 5% NH_4Br solution, and stabilized at 250°C by multistep annealing approach for different stabilization times (in each stage) (b) 5 min (c) 15 min (d) 30 min (e) 45 min (f) 60 min (g) 75 min.

The infrared spectra of stabilized PAN fiber show major structural transformations as reflected in the intensities of the IR spectra with increasing stabilization time. The comparison of infrared spectrums in the area of 2000–450 cm^{-1} of unmodified and heat stabilized PAN multifilament fibers impregnated with NH_4Br for different treatment times is presented in Fig. 6. A close examination of the IR spectrums presented in Fig. 6 indicates important structural transformations compared to the spectrum of the original PAN specimen. After a stabilization time of 5 min, the carbonyl ($\text{C}=\text{O}$) vibration spectrum of aliphatic ketone vibration at 1736 cm^{-1} weakens in strength and moves to a lower position by increasing processing time till it is clearly visible as a significant conjugation absorption (Fig. 6). Because of the structural changes occurring during the thermal stabilization process, a new vibration at about 1585 cm^{-1} is observed in the IR spectrum of NH_4Br impregnated and heat stabilized PAN sample. The infrared band positioned at 1585 cm^{-1} is thought to be an indication of intramolecular reactions as well as the transformation of nitrile ($\text{C}\equiv\text{N}$) group into nitrile ($\text{C}=\text{N}$) band due to the development of aromatization processes (Karacan and Erdogan, 2012). The spectrum develops further with increasing stabilization time (Fig. 6). This characteristic feature was mentioned as a possible sign of becoming a part of the conjugated structure of the carbonyl bands (Grassie and Mcguchan, 1972). During the thermal stabilization process, the $\text{C}-\text{C}$ single bond is converted into a $\text{C}=\text{C}$ double-bonded species that forms aromatic structures, where oxygen is assumed to play a key role by assisting dehydrogenation reactions (Ouyang et al., 2008).

4. CONCLUSIONS

In this study; The stabilization phase was accelerated by using the chemical pretreatment method. Therefore, it is aimed to shorten the carbon fiber production time and to reduce the energy consumption cost. As a result of the experiments; changes in color were observed in most of the samples after stabilization. It was observed that it gained full blackening and non-flammability in 30 min, 45 min, 60 min, and 75 min. We observed this behavior as an indicator of cyclization in the molecular structure. Physical and chemical changes were observed in the samples during thermal stabilization. It has been observed that NH_4Br salts accelerate the thermal stabilization reactions in the PAN polymer. Fiber characterization techniques; TGA, FT-IR, and XRD analysis methods were used. Additionally, an optical microscope was used to measure the fiber thickness of the samples. TGA analysis

results indicated thermal stability of chemically pre-treated stabilized PAN samples compared to raw PAN polymer. At the same time, it was observed that mass loss decreased and carbon yield increased in parallel with the enhance in heat treatment time. The carbon yield of the raw PAN polymer which is 45%, increased by 72% in 75 minutes as a result of chemical pre-treatment and annealing. In the FT-IR analysis, it was studied in the mid-infrared region of 4000-450 cm^{-1} wavenumber range. In the results of the analysis of infrared spectroscopy (FT-IR) data, raw PAN and stabilized pan samples were compared. It was observed that the characteristic peaks of the raw PAN polymer decreased and disappeared with the increase of the heat treatment temperature. Samples with a changed molecular structure formed cross-links as a result of the processes. As a result, C = C bonds increased. They have a more thermally stable structure. As a result of XRD analysis, (100) and (110) reflections arising from the hexagonal structure are seen. Because PAN polymer unit cells consist of hexagonal crystal structure. According to the XRD analysis results, structural changes were observed in the PAN polymer depending on the heat treatment temperature. PAN samples lost their crystalline structure and turned into an amorphous structure. It decreases due to the increase in stabilization time and finally almost disappears at the stabilization time of 75 min.

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