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THERMAL OXIDATION OF POLYACRYLONITRILE FIBERS IN CARBON FIBER MANUFACTURING

KARBON LİF ÜRETİMİNDE POLİAKRİLONİTRİL ELYAFLARIN TERMAL OKSİDASYONU

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ABSTRACT

Thermal oxidation of polyacrylonitrile (PAN) fibers was accomplished at temperatures up to 250°C for different oxidation times. Chemical integration of PAN fibers with an aqueous solution of ammonium persulfate was performed before starting thermal oxidation. The results recommend that ammonium persulfate integration enhanced the oxidation reactions of the PAN fibers and resulting in enhanced thermal stability. Ammonium persulfate impregnation followed by the oxidation process in the air environment leads to significant deviations in the characteristics of PAN fibers. To perform structural characterization of the raw and ammonium persulfate (APS) incorporated and stabilized samples, XRD, IR-spectroscopy, TGA was executed in this study. Investigation of the XRD and infrared spectroscopy outcomes recommended quick aromatization reactions with growing oxidation periods. The TGA traces indicated a comparative enhancement in the thermal stability of the PAN fibers by the increased carbon yield with the rise of the oxidation time. The overall findings recommend that ammonium persulfate incorporation was very influential in stimulating the oxidation process.

Keywords: Polyacrylonitrile, Oxidation, XRD, TGA, IR-spectroscopy.

ÖZET

Poliakrilonitril (PAN) liflerinin termal oksidasyonu, farklı oksidasyon sürelerinde 250°C'ye kadar sıcaklıklarda gerçekleştirilmiştir. PAN liflerinin sulu bir amonyum persülfat çözeltisi ile kimyasal entegrasyonu, termal oksidasyona başlamadan önce yapıldı. Sonuçlar, amonyum persülfat entegrasyonunun PAN liflerinin oksidasyon reaksiyonlarını arttırdığını ve termal stabilitenin artmasıyla sonuçlandığını önermektedir. Amonyum persülfat emdirme işleminin ardından hava ortamında oksidasyon işlemi PAN liflerinin özelliklerinde önemli sapmalara yol açmaktadır. Ham ve amonyum persülfat (APS) içeren ve stabilize edilmiş numunelerin yapısal karakterizasyonunu gerçekleştirmek için bu çalışmada XRD, IR-spektroskopisi, TGA gerçekleştirilmiştir. XRD ve kızılötesi spektroskopi sonuçlarının araştırılması, artan oksidasyon periyotları ile hızlı aromatizasyon reaksiyonları önerdi. TGA izleri, oksidasyon süresinin artmasıyla artan karbon verimi ile PAN liflerinin termal stabilitesinde karşılaştırmalı bir gelişme gösterdi. Genel bulgular, amonyum persülfat katılımının oksidasyon sürecini uyarmada çok etkili olduğunu göstermektedir.

Anahtar Kelimeler: Poliakrilonitril, Oksidasyon, XRD, TGA, IR-spektroskopisi.

1. INTRODUCTION

Carbon fibers are currently widely regarded as one of the most durable and lightweight reinforcing elements for revolutionary composite materials[1]. Because of its superior tensile capabilities and low-density value, carbon fiber in the form of a composite stands out as a prominent element for a variety of sophisticated and high-volume applications. Carbon fiber manufacturing sectors are growing at a rapid rate, with applications in automobile, aviation, military, sports, medical, and construction materials[2,3]. In the carbonization phase of carbon fiber manufacture, oxidation of the precursor fiber is a very essential phases for making the precursor fiber infusible[4,5].

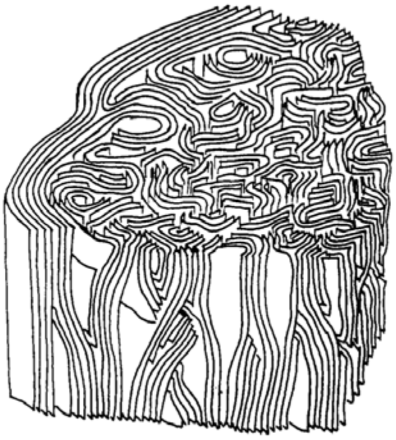

Fig. 1. Schematic representation of carbon fiber structure[6].

In carbon fiber manufacturing, many precursor fibers are employed. Carbon fibers may also be made from mesophase pitch, in addition to cellulose and polyacrylonitrile (PAN) precursors. Because of the poor carbon yield and inferior tensile characteristics, cellulose-based carbon fibers have lost credibility[7–9]. Although the majority of carbon fibers are now manufactured from polyacrylonitrile (PAN) precursor due to its higher tensile properties and yield values, carbonization of organic fibers is still the most feasible way of manufacturing carbon fibers[10]. In the thermal-oxidation stage, PAN fiber is heated from 250 to 350°C for one hour or more to transform it into an infusible fiber. Following this phase, the PAN fibers are heated in the inert atmosphere to carbonize at a temperature of 1000 to 2500°C, which is known as the carbonization temperature[11–13].

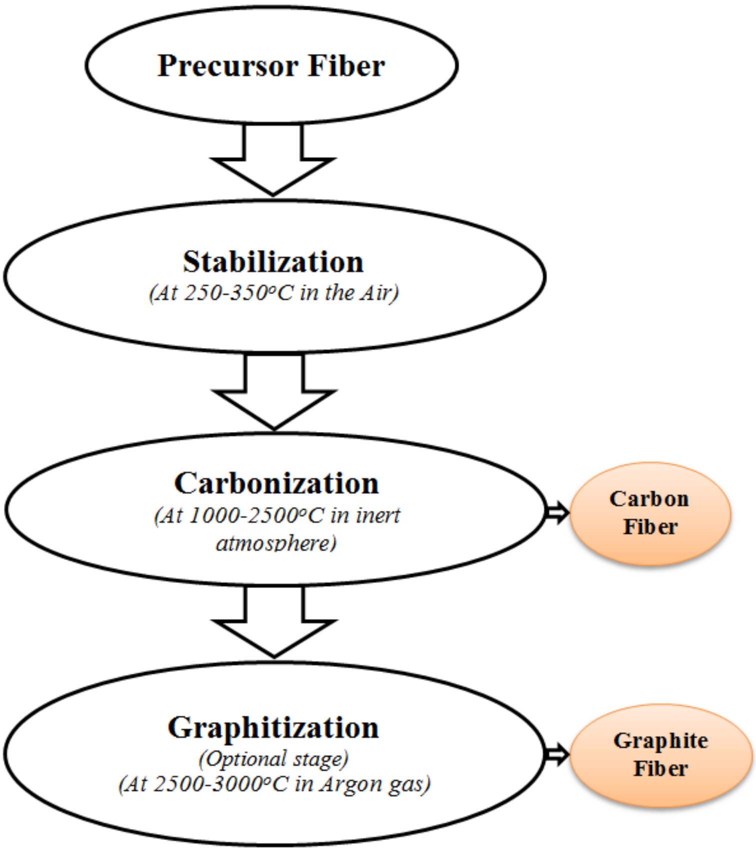

Fig. 2. Process flow of carbon fiber manufacturing

The stabilized PAN samples become infusible prior to the carbonization cycle[14]. To minimize or restrict chain breakage during the carbonization process, polyacrylonitrile molecules must be linked together or their inherent stiffness must be enhanced[15,16]. The comonomer functions as an activator in the oxidation process[17]. The oxidation rate of the PAN fiber is regulated by applied tension, temperature, and copolymer composition, according to several studies[18,19].

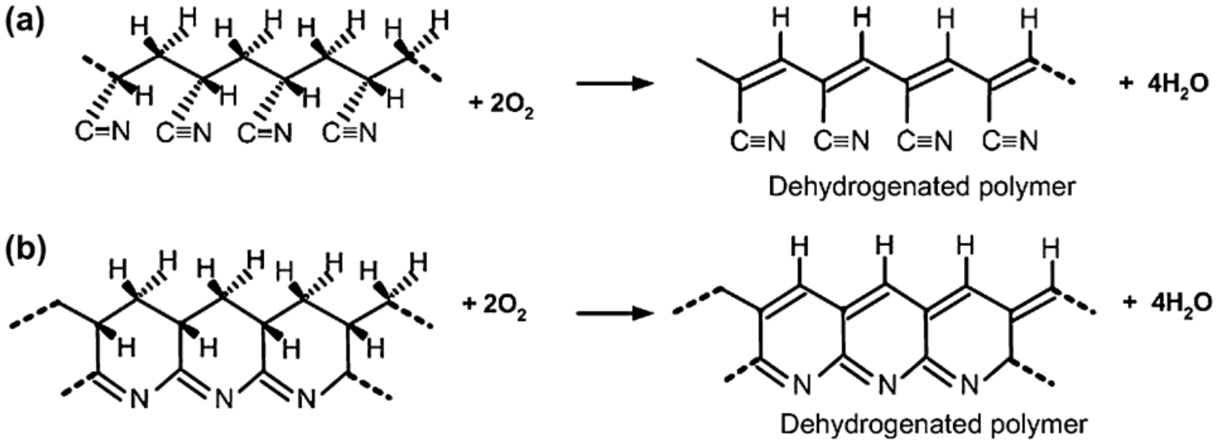

Fig. 3. The dehydrogenation reaction in the oxidation process. (a) PAN polymer; (b) cyclized PAN[20].

The PAN's chemical structure is altered during the oxidation process, making it more thermally stable[21]. The transformation of the PAN sample into an infusible unchanging ladder structure is also influenced by this process. It causes cross-linking between the PAN structures, allowing it to work at high temperatures with minimal carbonaceous material volatilization[22,23]. The ladder ring construction was meant to enhance the dark color of the oxidized PAN sample[25]. In the whole oxidation progression, the heating rate, cooling rate, the maximum temperature, and the oxidation time keep vital importance in changing the whole stabilization process outcome of the PAN fibers[21,26–29]. The influence of ammonium persulfate integration for improving the oxidation process was investigated in depth in this research. The goal of this study was to see how ammonium persulfate pretreatment influenced the molecular level of oxidized PAN fiber earlier to carbonization.

2. SAMPLE PREPARATION

In this investigation, polyacrylonitrile fiber was employed as a precursor fiber for the thermal oxidation process. Ammonium persulfate was utilized for the pretreatment of the precursor fibers prior to the oxidation step. APS has the characteristics to quicken the oxidation phase while used in proper experimental conditions. APS is thought to demonstrate the quickening process in the oxidation due to the attendance of free radicals, SO_4^- and H_2O_2[30,31]. Superficial dirt of the raw sample was eliminated by soaking it in a solution of perchloroethylene and isopropyl alcohol for 40 minutes at 25°C before initiating chemical impregnation. Chemical processing of the PAN saple was accomplished by immersing the samples in a 15 percent aqueous APS solution for 24 hrs. At 20°C, the pH of the solution was 2.5. On a dry basis, the pretreated PAN comprised 10.68 percent (w/w) APS.

3. APPLIED METHODS

3.1 Valuation of X-ray Diffraction (XRD) Analysis

X-ray profiles were attained by a Bruker AXS D8 model XRD machine. Counting was done at a rate of 10 steps per degree. For both original and thermally stabilized materials, X-ray diffraction data were acquired between 5–35° 2θ, and incoherent scatter, Lorentz, and polarization factors were adjusted[32].

3.2 Valuation of Thermo-gravimetric (TGA) Analysis

The TGA profiles of the pristine and oxidized PAN were obtained using a Perkin Elmer TGA scheme. The maximum temperature in the TGA studies was 1000°C, and a sample weight of approximately 5-6 mg. Temperature scaling of TGA was completed employing melting point benchmarks of gold, indium, aluminum, zinc, and tin.

3.3 Valuation of Fourier Transform Infrared (FT-IR) Measurements

FT-IR study was carried out using a Perkin Elmer FT-IR spectrometer. The average value was calculated using 50 interferograms and a Norton-Beer apodization algorithm. All the bands were ratioed by retaining unchanging device modifications.

4. RESULTS AND DISCUSSION

4.1 X-ray Diffraction Analysis

Figure 4 shows XRD profiles of pristine, APS incorporated and oxidized PAN samples for oxidation times ranging from 5 to 60 minutes. Double ordered points with d-spacing of 0.309 and 0.538 nm are ascribed to a hexagonal unit cell in the original polyacrylonitrile sample's equatorial X-ray diffraction curve[14,33,34]. The outcomes reveal that the (100) and (110) reflections of a hexagonal lattice with basal plane proportions of a = b = 0.6 nm may be attributed to the ordered maxima (PE1 and PE3)[14].

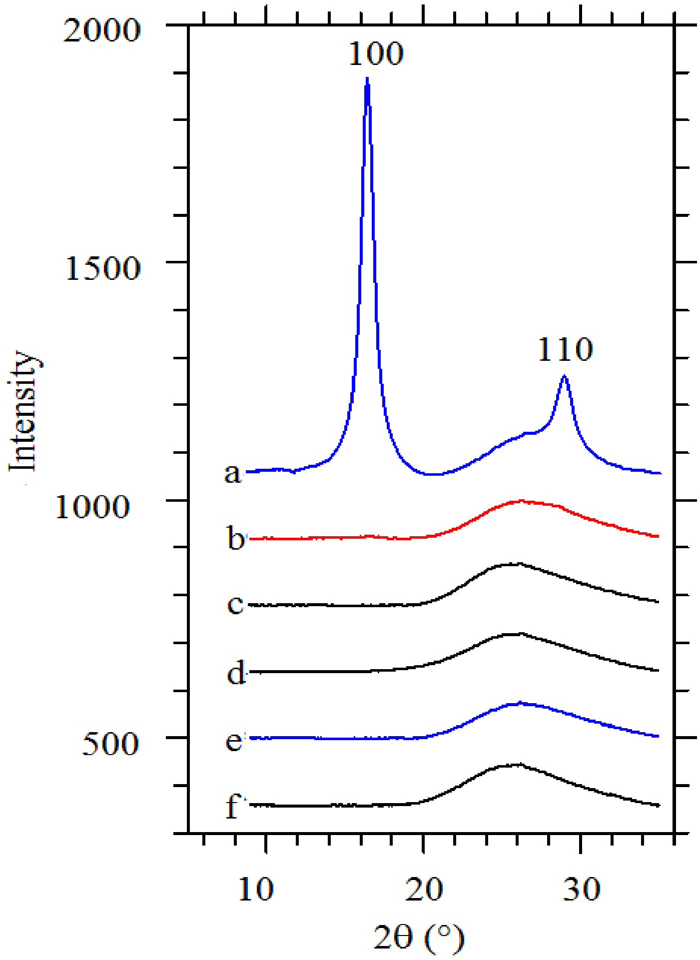

Fig. 4. X-ray diffraction profiles of original (a) and oxidized PAN samples for (b) 5 min; (c) 15 min; (d) 30 min; (e) 45 min; (f) 60 min.

In the diffraction pattern, there is an extra, lower ordered, and wide peak having a d-spacing of 0.346 nm (around 25.6° 2θ). The unoriented and chaotic phase can be attributed to this peak. The (002) reflection of the pre-graphitic construction (for example, aromatic or ladder) is responsible for the d-spacing of this point [14]. For the laterally organized structure, the thermal oxidation process appears to have a substantial influence on crystal structure via crystallite size and degree of crystallinity. Peak height, peak location, and half-height breadth are used in a curve-fitting technique to get accurate peak parameters[14,33,34]. A detailed examination of this analysis reveals that as oxidation processes continue, the hexagonal crystal state loses its laterally ordered arrangement[14,33,34]. The (100) reflection remains in the sample for the first 5 minutes of oxidation but vanishes absolutely for samples oxidized for 15 minutes or more.

4.2 Thermogravimetric Analysis (TGA)

The thermogravimetric method is usually employed to assess char yield (percentage), an important metric for heat oxidized materials. Thermally stabilized polyacrylonitrile samples lose weight during the carbonization stage by removing organic components as decomposition by-products. Hydrogen is usually eliminated as part of the water vapor in the dehydrogenation process. On the other hand, nitrogen is released in the form of hydrogen cyanide (HCN), nitrogen (N_2) gas, and oxygen is removed as carbon monoxide (CO), water (H_2O) vapor, carbon dioxide (CO_2), or simple oxygen (O_2) gas. TGA traces are illustrated in Figure 5 for pristine and oxidized PAN fibers. TGA curves show a decrease in weight loss as treatment time increases, indicating growth in carbon yield. Due to the formation of a greater number of cross-linking associated ladder structures, oxidized polyacrylonitrile loses weight over a broader range of temperatures. The untreated PAN, on the other hand, loses weight across a narrower range of temperatures. Heat oxidized samples between 300 and 450ºC undergo severe thermal degradation in 5 minutes, with weight loss of 63.5 percent at 500ºC and 56.6 percent at 1000ºC. Between 50ºC and 450ºC, the weight loss decreases as the oxidation duration lengthens (Figure 5). Weight loss for the thermally stabilized PAN fiber is 75.9% at 500ºC and 69.2% at 1000ºC after 60 minutes.

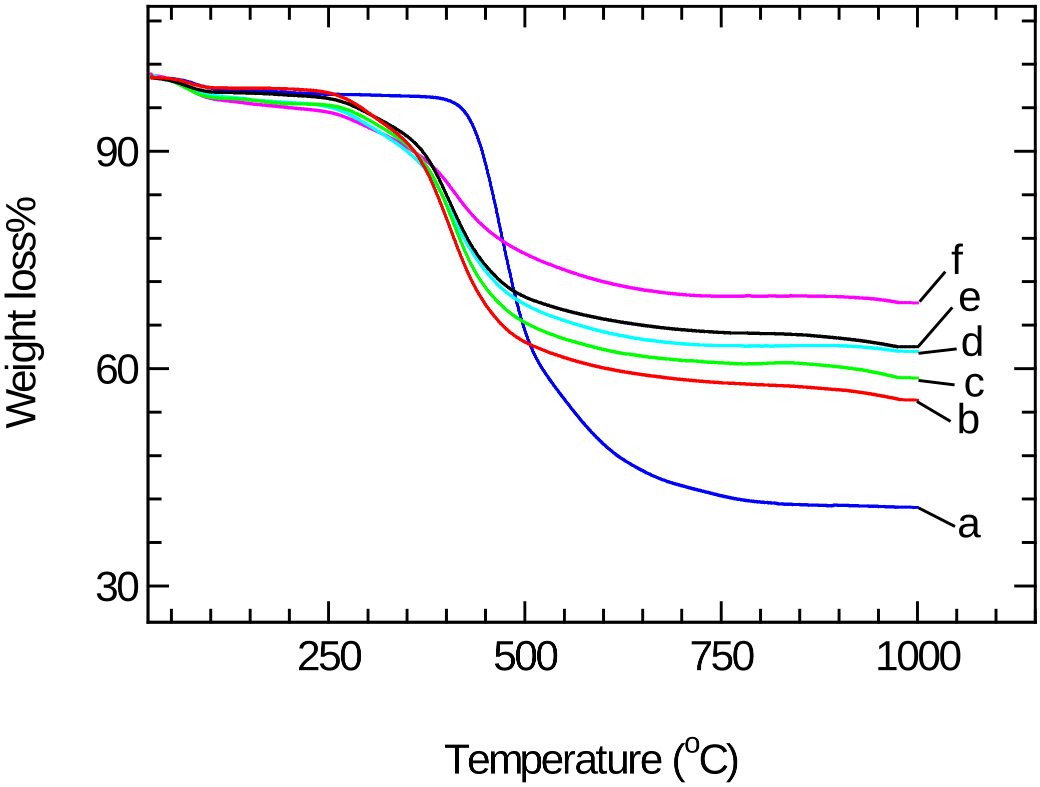

Fig. 5. TGA thermograms of original (a) and oxidized PAN fibers for different oxidation periods (b) 5 min, (c) 15 min, (d) 30 min, (e) 45 min, (f) 60 min.

4.3 FT-IR Spectroscopy Analysis

Infrared spectroscopy was used in this work to track structural and chemical changes that happened in the stabilization stage. Figure 6 compares the infrared bands in the range 2000–450 cm^{-1} of raw and oxidized PAN fiber pretreated with ammonium persulfate for different treatment periods. When compared to the pristine PAN vibration, the spectra show significant structural changes. The carbonyl stretching vibration at 1736 cm^{-1} loses much of its strength after 5 minutes of oxidation of PAN fiber and moves to a lesser band with growing stabilization period (Figure 6). This feature was proposed as a possible indicator of the carbonyl groups being conjugated[35].

The existence of APS is recognized by the vibrational frequencies at 1654, 1584, 1155, and 807 cm^{-1} in Figure 6. The infrared band at 1584 cm^{-1} is supposed to indicate intramolecular reactivity and the cyclization procedure, which transforms the nitrile group into the nitrilo group. Various assignments for this spectrum have been referenced in the existing literature. It is designated to conjugated nitrilo (C=N) units produced through cyclization in certain investigations.[35–37]. Clarke and Bailey categorize this spectrum as C=C and C=N groups[38]. The conjunction of C=C and C=N vibrations is likewise ascribed to this band[39,40]. Another assignment is the conjunction of C=N stretching, N–H, and C=C in-plane bending bands for oxidized PAN fibers[41].

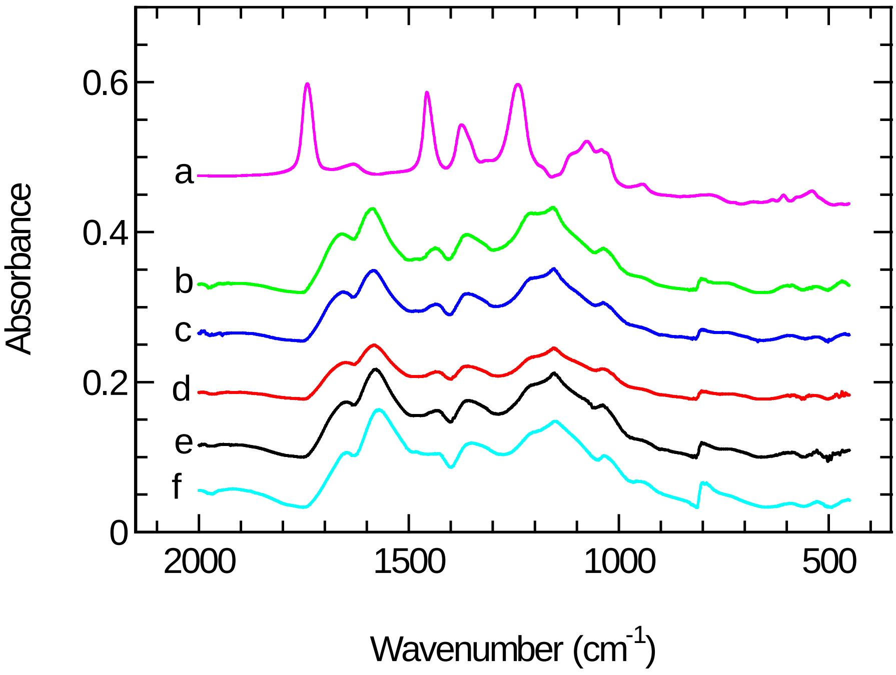

Fig. 6. IR-spectra in 2000–450 cm^{-1} range of original (a) and oxidized PAN fibers for (b) 5 min, (c) 15 min, (d) 30 min, (e) 45 min, and (f) 60 min thermal oxidation.

Because of the occurrence of dehydrogenation and the creation of C=C bonds, the CH_2 and –C–O stretch bands decrease their intensity and gradually become less dominating with increasing treatment time (Figure 6). The IR vibrations between 1600 cm^{-1} and 1300 cm^{-1} are categorized by the immense broadening and intensity growth by a new spectrum formation centered at 807 cm^{-1}, ascribed to a conjugated C=C–H vibration[42].

Between the wavenumber range 3000 cm^{-1} and 2800 cm^{-1}, two major spectra centered at 2920 cm^{-1} and 2852 cm^{-1} were shown in Figure 7. It shows the intensity fluctuation of the C≡N groups of the acrylonitrile monomers as a component of the PAN polymer as the oxidation duration increases. A nitrile vibration is located at around 2242 cm^{-1}. The methylene (CH_2) spectra lost their supreme intensity after only 5 minutes of oxidation, indicating hydrogen atom removal due to dehydrogenation processes happening in the polymer chain. This is thought that throughout the oxidation process, oxygen is partially integrated with the samples because of dehydrogenation processes.

The nitrile absorption band at 2242 cm^{-1} shows a rapid intensity decrease in Figure 7. A distinct spectrum linked with thiocyanate (S=C=N) stretching emerges at 2120 cm^{-1} [43]. Another new vibration appears at 2200 cm^{-1}, which is linked to nitrilo conjugation and the ionic constructions[35]. The α,β-unsaturated, and β-imino nitrile groups that arise from dehydrogenation processes or through the tautomerization and isomerization of the ladder structure are thought to be responsible for this spectrum allocation[44,45].

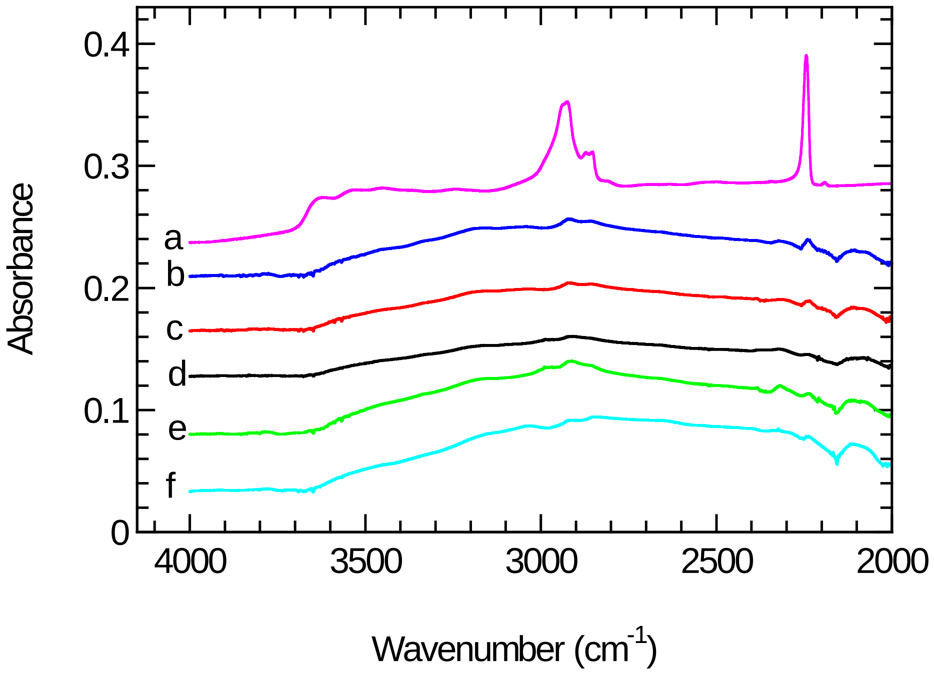

Fig. 7. IR-spectra in the 4000–2000 cm^{-1} range of original (a) and oxidized PAN fibers for (b) 5 min, (c) 15 min, (d) 30 min, (e) 45 min, and (f) 60 min thermal oxidation.

Stabilized samples reveal a larger intensity fall of nitrile groups in oxygen-rich air than at increased temperatures[38]. After the 60-minute multi-step heating, the bands spanning 3700 and 2300 cm^{-1} include an identical prominent height of 2920 cm^{-1}. The loss of hydrogen atoms causes dehydrogenation processes in the cross-linked polymer chains, as seen by the steady intensity loss of the methylene spectrum at 2920 cm^{-1}.

5. CONCLUSIONS

The experimental results demonstrate that ammonium persulfate pretreatment optimizes the oxidation time and aids in the rapid development of the cyclized structure. PAN samples had considerable physical and structural changes as a result of the oxidation process in the air. Infrared data demonstrated a quicker cyclization and dehydrogenation process when the oxidation duration was increased. The rapid intensity reduction of the nitrile band at 2242 cm^{-1} and the methylene band at 2920 cm^{-1} confirms this concern. The TGA profiles revealed a reasonable progress in thermal stability as the oxidation period progressed, which was assessed by the rise in carbon production. PAN fibers that have been oxidized at 250°C for 60 minutes are expected to tolerate higher temperatures during the carbonization step. The integration of ammonium persulfate with PAN fibers in carbon fiber manufacture speeds up the oxidation process that lowers the total processing budget of carbon fiber production.

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