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A COMPARATIVE STUDY OF STRUCTURE AND PROPERTIES OF THE THERMALLY STABILIZED PA6 FIBERS PRETREATED WITH AQUEOUS AND ETHANOL SOLUTION OF 1% FERRIC CHLORIDE ($FeCl_3$) BEFORE CARBONIZATION

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ABSTRACT

An experimental study was carried out on incorporating ferric ions (Fe^{+3}) in thermally stabilization reactions of polyamide PA6 fibers. The structure and properties of the thermally stabilized PA6 fibers were determined by fiber diameter, volume density, tensile testing, oxygen content (%), infrared spectroscopy (FT-IR), and thermogravimetric (TGA) analysis measurements. The accelerator effect of ferric chloride ($FeCl_3$) impregnation was beneficial for performing thermal stabilization experiments before the carbonization stage. 1% Ferric chloride pretreated, and thermally stabilized PA6 fibers have been reported to decrease fiber diameter and linear density values. FT-IR analysis indicated rapid and concurrent aromatization and dehydrogenation reactions assisted by the formation of oxygen-containing functional groups. TGA thermograms have shown a relative improvement in thermal stability, as shown by increasing carbon efficiency over time. A thermal stability improvement was observed using TGA measurements. The carbon yield of the ferric chloride impregnated 120 min stabilized PA6 fibers reached a maximum of 58% at 1000°C. FT-IR and TGA measurements show improved thermal stability when ferric ions (Fe^{+3}) have been incorporated into the polymer structure. The formation of ferric ionic bonds has improved thermal stabilization by promoting aromatized and cross-linked structures. Experimental results suggest that ferric chloride incorporation has been highly effective and effective in promoting thermal stabilizing reactions.

Keywords: PA6 Fibers, Thermal Stabilization, $FeCl_3$, FT-IR, TGA

ABBREVIATIONS

CF : Carbon Fiber; **CFs :** Carbon Fibers; **CFRP :** Carbon Fiber Reinforced Polymer; **PAN :** Polyacrylonitrile; **TOS :** Thermal Oxidative Stabilization; **Tg :** Glass transition temperature; **PA:** Polyamide; **PAs :** Polyamides; **PA6 :** Polyamide 6 or Polycaproamide or commercial name is Nylon 6; **$FeCl_3$:** Ferric chloride; **$FeCl_2$:** Ferrous chloride

1. INTRODUCTION

CFs consisting of at least 92% carbon by mass [1, 2] have a regular hexagonal microstructure [2]. CFs are widely used because of their low weight, low density, and high chemical resistance [3]. First developed in the 1960s, CF is still considered one of the most essential materials in modern-day science and technology [4]. CFs are used as reinforcement elements in Polymer, metal, and ceramic matrixes to be composites [1]. These CFRP composites have increasing aerospace, automotive, sporting goods, biomedical applications, and defense industries [5-10].

PAN, the basic raw material for precursor fiber manufacturing technology, is synthesized from oil and natural gas [11]. Aliphatic polyamide fibers were also utilized as precursors to prepare carbon fibers [12-15]. Heat treatment of the fibers (stabilization and carbonization) accounts for 69% of the total energy consumed during manufacture, with 48% being consumed during the fiber stabilization step and 21% during the fiber carbonization step. This results in promising potential energy savings [15]. The primary untreated material of CFs is 90% PAN-based fibers, 10% viscose rayon-based fibers, and petroleum pitch-based fibers [16]. CF production has two critical steps in the industry [16]. The first step is thermal stabilization processing, and the second step is carbonization processing; a graphitization stage is an optional activation stage [1, 2, 17, 18]. The three processes are shown in Fig. 1 [10, 19-22].

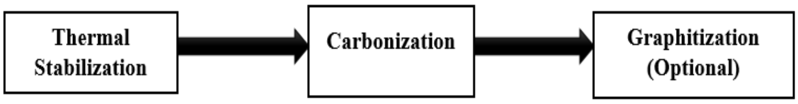


Fig. 1. Flow chart of carbon fiber production stages [10, 19-22]

The precursor fiber converts to a golden blonde color throughout stabilization, followed by a deep brown color, and finally a dark black color [23]. 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 [24, 25]. Consequently, linear polymer chains are transformed into cyclic or ladder-type structures, keeping non-flammable fibers when carbonized at higher temperatures [17, 26]. In short, with the development of the stabilization reactions, the tensile strength was lowered due to the diminishing cohesive energy between the molecular chains [27]. Increasing the amount of oxygen in the atmosphere has increased the density of the fiber. The tensile strength is reduced as the number of oxygen increases [28, 29]. Precursor fibers are obtained with high-temperature tolerance and fireproof properties in the stabilization stage [16, 17]. The carbonization process, which removes almost all non-carbon atoms from the molecules, is an inert gas. It consists of two stages, a pre-carbonization process at 400-600°C and a primary carbonization process at 600-1300°C [2, 17, 19, 30]. According to Takaku et al., it seems that high-density values of stabilized samples result in CFs with low tensile strength values due to the formation of micro-pores [18]. The most common synthetic PAs are often referred to as nylons (the manufacturer's trade name, DuPont), and they are aliphatic PAs [31, 32]. PA6 polymers heated at 150°C for 5 hours in dry air deteriorate, lose their shine and turn yellow. The relatively low melting point of PA6 fibers means they cannot be used at high temperatures. PA6 melts when heated above 214°C [33]. Stabilization was performed at 170°C within 43 hours to render the PA6 Polymer non-flammable without the need for chemical processes. As a result, PA6 Polymer developed flame-retardant and thermosetting properties. After 2 hours of oxidation at 170°C, the PA copolymer lost its thermoplastic properties [12]. Commonly, the dehydrogenation of the Polymer occurs, which then results in cross-linking. As a result, Lewis acid-type transition metal chloride ($MeCl_x$) may act as an effective cross-linking catalyst [34]. Lately, efforts have been made to study metal ions for polymer flame retardant and eco-friendly [35-38]. $FeCl_3$ (anhydrous) is also known as iron (III) chloride. Inorganic salt is used as a catalyst and oxidation agent. It is acidic in water. It is a perfect source of water-solvable crystal iron for chloride-coherent applications. It is soluble in organic solvents, especially in ethanol. At least one chloride anion (Cl^-) is formed with various chlorinations and is covalently bound to the respective metal or cation. Equation (1) by using the $FeCl_3$ aqueous solution equation is defined as follows [39, 40-44]:

$$FeCl_{3\,(s)} + H_2O_{(aq)} \rightarrow [Cl_3FeOH_2]_{(aq)} \rightarrow [Cl_3FeOH]^-_{(aq)} + [H^+]_{(aq)} \quad (1)$$

$$FeCl_{3\,(s)} + C_2H_5OH_{(aq)} \rightarrow [Cl_3FeHOH_5C_2] \rightarrow [Cl_3FeOH_5C_2]^-_{(aq)} + [H^+]_{(aq)} \quad (2)$$

Equation (2) using the $FeCl_3$ ethanol solution equation is defined as follows: Ethanol (C_2H_5OH) is referred to as ethyl alcohol or pure alcohol. It consists of a group of organic chemicals in which the molecules involve a hydroxyl group, -OH, bound to a carbon atom [45].

The research investigates the outcome of $FeCl_3$ salt impregnation in the TOS of PA6 fibers before carbonization. They have been shown to accelerate TOS before carbonization, the degree of which has been determined by measuring fiber diameter, linear density, volume density, tensile strength, TGA, and FT-IR analysis. The density changes that result from stabilization have already been looked at in detail for our experiment. The present investigation finds melt-spun PA6 fibers as one of the most suitable precursors to manufacture carbon fibers.

2. MATERIAL AND METHODS

The molecular structural model of untreated (original) PA6 is shown in Fig. 2 [46].

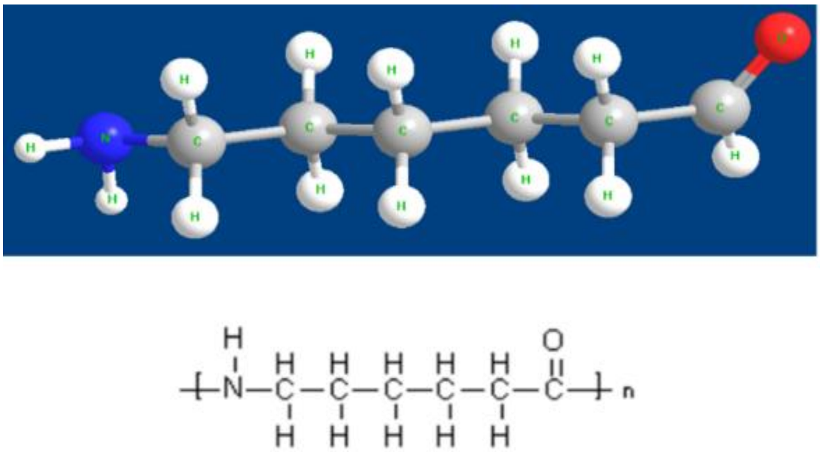


Fig. 2. Chemical structure of untreated PA6 [46]

2.1. Materials

The carbon content (C) of the PA6 Polymer is 66.06%, the nitrogen content (N) is 12.84%, the hydrogen content (H) is 10.09%, and the oxygen content (O) is 11.01%. Commercially available PA6 precursor multifilament fiber was used during the experimental work, which was supplied by the Anatolia Yarn and Textile Factories Company (Tekirdağ-Turkey). These PA6 precursors (untreated) fibers have a linear density of 15.83 ± 0.05 Tex per 48 filaments together with a fiber thickness of 19.85 ±0.3 μm.

2.2. Fiber Impregnation and Fiber Stabilization Methods

Untreated PA6 fibers were washed with an aqueous 10% ethanol solution for 60 minutes to remove surface impurities. Afterward, it was cleaned under running water for half an hour. Fig. 3 illustrates the process used during the TOS. 1% (w/w) $FeCl_3$ aqueous solution and 1% (w/w) $FeCl_3$ ethanol solution were used to impregnate and compare PA6 fibers. The value of the 1% (w/w) $FeCl_3$ aqueous solution was measured at pH = 1.93 to 20 ºC and The value of the 1% (w/w) $FeCl_3$ ethanol solution was measured at pH = 1.53 to 20 ºC. The alcohol (ethanol) solution was observed to increase the acid content concerning the aqueous solution. The 1% (w/w) $FeCl_3$ ethanol solution impregnated with linear density PA6 fibers is 17.27 ± 0.21 Tex, and the percent load of these fibers is + 8.97 %. The 1% (w/w) $FeCl_3$ aqueous solution impregnated PA6 fibers of linear density value is 17.64 ± 0.59 Tex, and the percentage of loading on the fibers is +11.43%. The linear density of the impregnated PA6 sample increased from the untreated PA6 fiber (15.83 ± 0.05 Tex). PA6 fibers absorbed more metal salt in the ethanol solution than in the water solution. Table 1 illustrates the process used during thermal stabilization.

Table 1. PA6-based stabilized fiber production flow chart

Experimental order
1. Untreated PA6 fibers
2. Impregnation of 1% $FeCl_3$ aqueous solution in 20 ºC at 24 h
3. Dry at 80°C for 2 h in an oven (heating rate 1°C/min)
4. Dry at fixation temperature 140°C for 45 min in an oven (heating rate 1°C/min)
5. Firstly, in the stabilization period, from 20 to 170°C was increased at a heating rate 2°C/min. Stabilization is waiting in air at 245ºC (heating rate 0.3 ºC/min) at 30, 60, 90, and 120 min different times
6. Fibers characterization (TGA, FT-IR) analysis

During the heating experiments, the untreated PA6 fiber samples were wrapped on rectangular stainless steel frames to prevent shrinkage and reduction of fiber orientation. Finally, the TOS of the PA6 fibers was carried out in a circulation furnace. X min* has a variable value. Displays the stabilizing time in minutes for each stage. Over the original PA6 fibers, 30, 60, 90, 120 min is applied individually. The temperature starts from 20°C. Raise the temperature from 20°C to 170-245°C and decrease with slow cooling to 20°C in Fig. 3.

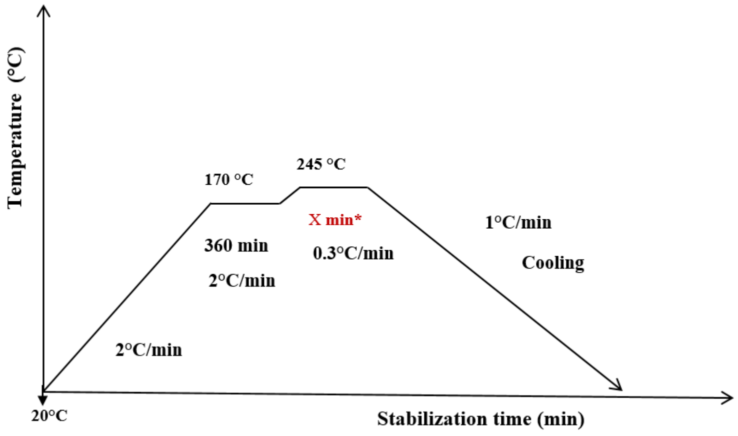


Fig. 3. Steps for annealing PA6 fibers impregnated 1% $FeCl_3$ (aqueous or ethanol) solutions

Fig. 4(a) shows how the iron atom interacts with the amide bonds of the polymer PA6 with the effect of heat. By forming a complex between PA6 hydrogen radicals and iron, they became connected through cross-linking. As a result, these cross-links increase the thermal resistance and non-flammability properties. The formation of cross-linking reactions in PA6 Polymer during stabilization is shown in Fig. 4(b).

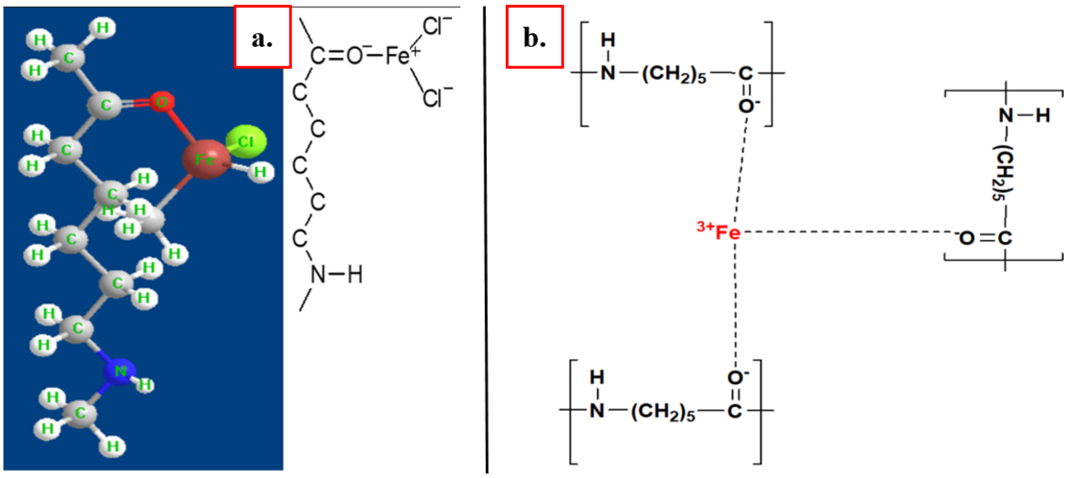


Fig. 4. **(a.)** Bonding form of ferric chloride metal halogen to the oxygen atom (PA6) **(b.)** Formation of cross-linking reactions in polymer PA6 during stabilization

3. RESULTS AND DISCUSSION

TOS is a critical stage before the carbonization phase that allows the precursor fibers to endure higher temperatures in the carbonization process. At the later stage, the dark color conversion confirms the existence of a thermally stabilized sample structure.

3.1. Experimental Analysis Results

3.1.1. Color Change stage and Non-flammability test

Color changes during thermal pre-treatment of PA6 fibers in the air may present the changes directly. In this way, it is proposed that reactions occurred during the thermal stabilization in the air circulation oven. As shown in Fig. 5, it is clear that the color of the fibers gradually changes from white to dark brown and black during the thermal stabilization in an air circulation oven.

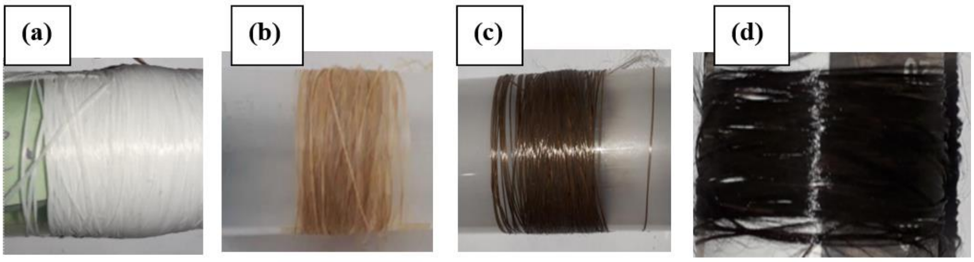


Fig. 5. Color changes of PA6 (a) Original fibers (white) during TOS stage in air-circulating oven, (b) 1% (w/w) $FeCl_3$ aqueous solution (c) Heating 170 °C at 2 °C /min holding for a given stabilization time (360 min) for 1% (w/w) $FeCl_3$ aqueous or ethanol solution (d) Heating 245°C at 0.3°C /min holding for a given stabilization time

In flammability testing, the inherent resistance of polymers to combustion was the principal factor affecting fibers' performance, with weight, weaving, and diameter being secondary. The availability of oxygen in the air is also a crucial factor in determining the flammability of fibers. As the stabilization time increases, the non-flammability of the fibers increases (Fig. 6).

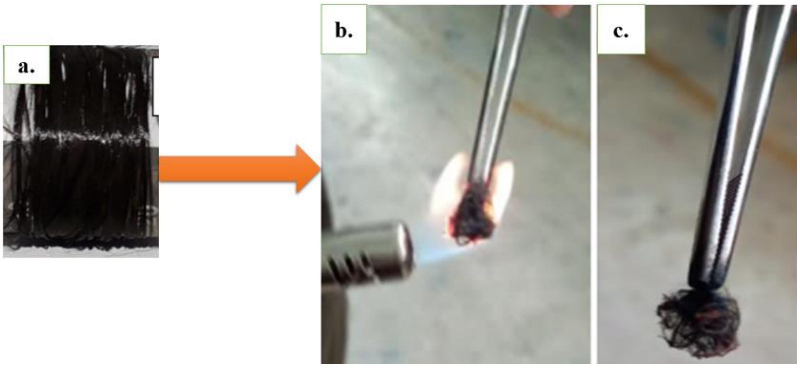
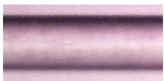


Fig. 6. The flame test applied to PA6 fibers after stabilization times. a) Stabilized PA6 fibers, b) Non-flammability test, c. Non-flammable and infusible

Results for these tests are presented in Table 2. Non-flammable properties were achieved at stabilization times of 60, 90, and 120 min. The fiber color turned utterly black after the 30 min stabilization period. The same color changes were observed at 170 and 245°C in both PA6 fibers impregnated in 1% $FeCl_3$ aqueous and alcohol solutions. However, the non-flammable and strength properties of the 1% $FeCl_3$ aqueous solution were higher than those of the alcoholic solution. Therefore, the fiber characterization analyzes of the aqueous solutions were performed in detail.

Table 2. Non-flammability test with 40x magnification in the optical microscope

1% (w/w) $FeCl_3$ ethanol solution				**1% (w/w) $FeCl_3$ aqueous solution**			
Stabilization time at 245 °C (min)	**Color change**	**Image of fiber color (40X)**	**Non-flammability test**	**Stabilization time at 245 °C (min)**	**Color change**	**Image of fiber color (40X)**	**Non-flammability test**
Untreated	White		Fail	**Untreated**	White		Fail
15	Blackish		Fail	**15**	Blackish		Fail
30	Black		Fail	**30**	Black		Fail
60	Black		Fail	**60**	Black		Pass
90	Black		Pass	**90**	Black		Pass
120	Black		Pass	**120**	Black		Pass

3.1.2. Linear Density, Volume Density, Fiber diameter Properties

The change of linear density values of original and stabilized PA6 samples impregnated in 1% $FeCl_3$ solution are illustrated in Fig. 7. The parameter that directly affects the linear density values is the stabilization time. The upper limit for linear density reduction was determined after 120 min of stabilization in a 1% $FeCl_3$ ethanol solution.

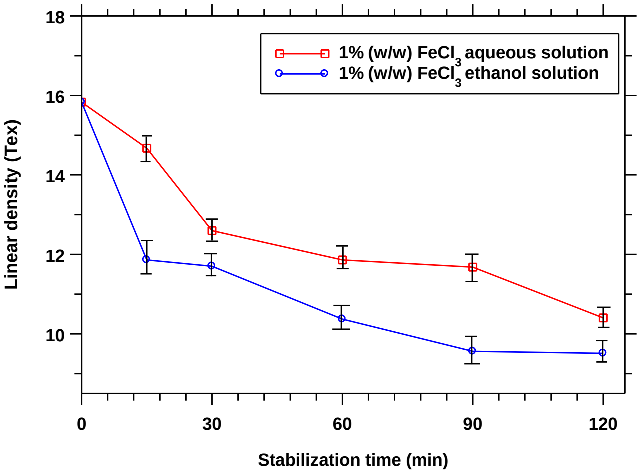


Fig. 7. Comparison of original and stabilized PA6 fibers in the effect of stabilization times (untreated, 15, 30, 60, 90, 120 min)

The untreated PA6 fibers have a linear density of 15.83 Tex. The linear density of PA6 fibers impregnated in 1% $FeCl_3$ aqueous solution with 15 min stabilization period was 14.67 Tex. The maximum amount of reduction in linear density was identified after 120 min stabilization time with a linear density of 10.40 Tex compared to the 1% $FeCl_3$ impregnated PA6 fiber. The linear density of PA6 fibers impregnated in 1% (w/w) $FeCl_3$ in ethanol solution and thermally stabilized for 15 min was found to be 11.86 Tex. The linear density of the PA6 sample stabilized for 120 min was found to be reduced to 9.51 Tex. As a result, the linear density of the PA6 samples impregnated in an alcoholic solution was found to be significantly reduced, possibly due to the adverse effects of the acidic solution.

The thermal stabilization stage is thought to result from a possible mass loss due to the thermal decomposition reaction that can occur during stabilization reactions. Fig. 8 presents the volume density values for the original (white) and thermally stabilized PA6 fibers, which were impregnated in $FeCl_3$ solution and stabilized for variable times ranging from 15 to 120 min. A continuous increase of density values is observed between 15 and 120 min stabilization times. The density of the original PA6 fiber is 1.14 g/cm^3. The density values increase from 1.14 to 1.39 g/cm^{3,} as illustrated in Fig. 8, because of ongoing cyclization and thermal stabilization reactions.

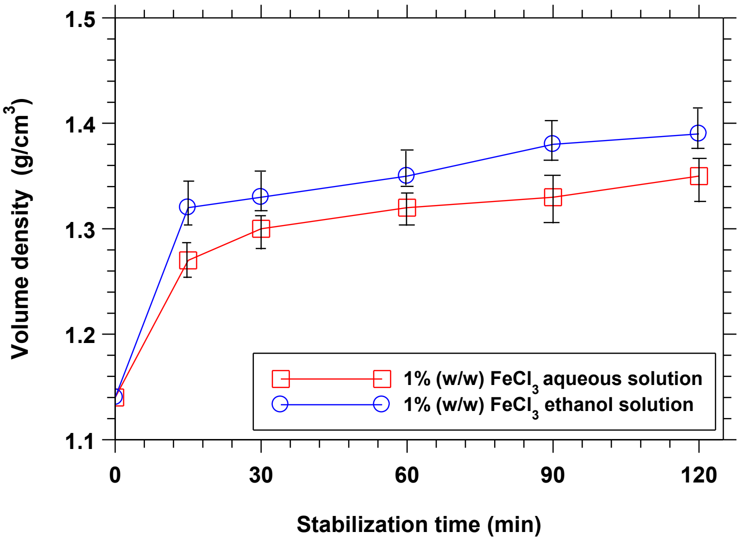


Fig. 8. Volume density (gr/cm^3) of untreated (white) and thermally stabilized PA6 fibers

The change of fiber diameter values of original and stabilized PA6 samples impregnated in 1% $FeCl_3$ aqueous and ethanol solution are compared in Table 3. The parameter that directly affects the fiber diameter values is the stabilization time. In the stabilization phase, it has been observed that with the increase of the stabilization time, elemental oxygen taken up directly affects the chemical structure of the fiber. The fiber diameter value of 1% (w/w) $FeCl_3$ aqueous solution impregnated, and thermally stabilized PA6 for 120 min was reduced by -15.95 % and showed a continuous reduction with an increasing stabilization period (Table 3).

The fiber diameter declined continuously with the rise of the stabilization period. The rapid growth of the density values of PA6 stabilized fibers is attributed to the development of cyclization and intramolecular cross-linking reactions. The values of linear density, fiber diameter, and tensile strength decrease with the increasing stabilization period.

Table 3. Physical properties of original (white) and thermally stabilized PA6 fibers

1% (w/w) $FeCl_3$ aqueous solution			**1% (w/w) $FeCl_3$ ethanol solution**		
Stabilization time (min)	**Fiber diameter (µm)**	**Fiber diameter loss (%)**	**Stabilization time (min)**	**Fiber diameter (µm)**	**Fiber diameter loss (%)**
Untreated	20 ± 0.3	------	**Untreated**	20 ± 0.3	------
15	18.27 ± 0.05	- 8.65	**15**	15.89 ± 0.04	-20.55
30	17.23 ± 0.1	-13.85	**30**	15.35 ± 0.05	-23.25
60	17.05 ± 0.29	-14.75	**60**	14.47 ± 0.09	-27.65
90	16.93 ± 0.28	-15.35	**90**	14.40 ± 0.07	-28
120	16.81 ± 0.05	-15.95	**120**	13.93 ± 0.03	-30.35

3.1.3. Analysis of Elemental Oxygen Content (%)

Elemental analysis of C, H, N, and C/H ratios was performed by combustion in a TruSpec Micro Elemental Analyzer (Leco Corp., US). The oxygen content was evaluated by difference. The samples were combusted in a heated, oxygen-rich environment. As shown in Table 4, the elemental oxygen content (%) increased with increasing fiber density. The ethanol solution had a higher elemental oxygen ratio. The fiber diameter and linear density values were observed to decline with increasing oxygen content. The loss of hydrogen arises from the occurrence of dehydrogenation reactions during the thermal stabilization process.

Table 4. Density and oxygen content % values for the origin and stabilized PA6 samples

Stabilization time (min)	**1% (w/w) $FeCl_3$ ethanol solution**		**1% (w/w) $FeCl_3$ aqueous solution**	
	Oxygen content (%)	**Volume density (g/cm^3)**	**Oxygen content (%)**	**Volume density (g/cm^3)**
Untreated	**11.01**	1.14 ± 0.02	**11.01**	1.14 ± 0.02
15	**13.2**	1.32 ± 0.03	**11.8**	1.27 ± 0.01
30	**13.9**	1.33 ± 0.05	**12.3**	1.30 ± 0.04
60	**14.83**	1.35 ± 0.03	**13.2**	1.32 ± 0.03
90	**17.71**	1.38 ± 0.06	**13.7**	1.33 ± 0.05
120	**18.02**	1.39 ± 0.04	**14.62**	1.35 ± 0.06

3.1.4. Mechanical Properties of Stabilized PA6 Fibers

The values of tensile properties were evaluated by employing a PROWHITE tensile testing machine. The optimum values of 20 mm gauge length and 5 mm/min strain speed were used to evaluate the mechanical properties for the stabilized PA6 fibers in our experimental work. Fig. 9 and 10 respectively show the effect of the tensile strength and tensile modulus of 245°C on the stabilization period fiber samples.

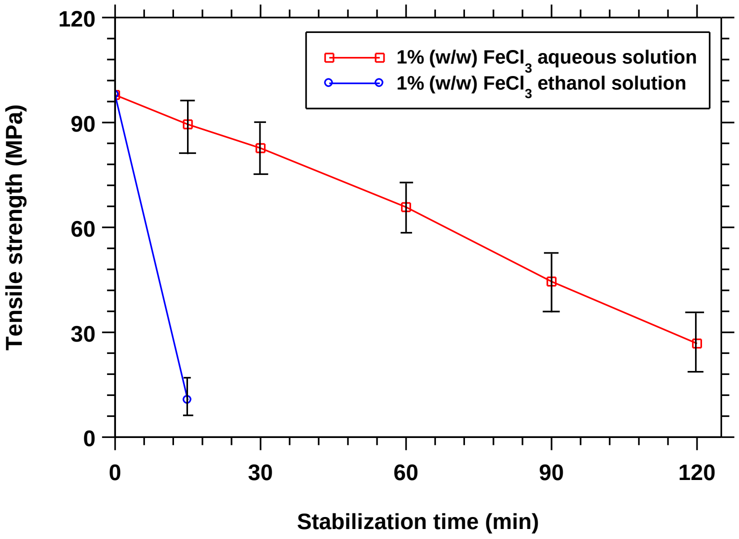


Fig. 9. Variation of the tensile strength of the original and thermally stabilized PA6 fibers according to the stabilization time (Untreated, 15, 30, 60, 90,120 min)

Untreated PA6 multifilament shows the highest tensile strength value of 97.84 MPa. During stabilization periods, there is a tendency to decrease tensile strength values. The tensile strength value of 15 min stabilized PA6 fibers impregnated in 1% $FeCl_3$ aqueous solution is 89.43 MPa, whereas for the PA6 fibers impregnated in 1% $FeCl_3$ ethanol solution, the tensile strength value is 10.57 MPa. Volume density of 15 min stabilized PA6 fibers impregnated in 1% $FeCl_3$ aqueous solution is 1.27 (gr/cm^3) and PA6 fibers impregnated in 1% $FeCl_3$ ethanol solution is 1.32 (gr/cm^3). The strength device did not detect other stabilization time values of stabilized PA6 fibers impregnated in ethanol solution. The tensile strength value of stabilized PA6 fibers impregnated in 1% $FeCl_3$ aqueous solution is 26.74 MPa, and the volume density was found to be 1.35 (gr/cm^3) during 120 min stabilization time. Therefore, as the stabilization time increases, density values increases, and tensile strength declines simultaneously.

The values of the tensile module are given in Fig. 10 for the untreated and thermally stabilized PA6 fibers. The tensile modulus value drops rapidly to about 5.85 GPa immediately after 15 min of multi-step annealing of the sample treated with 1% $FeCl_3$ ethanol solution. The tensile modulus value of 15 min stabilized PA6 fibers impregnated in 1% $FeCl_3$ aqueous solution is 12.05 GPa. The tensile modulus value of stabilized PA6 fibers impregnated in 1% $FeCl_3$ aqueous solution was found to be 7.91 GPa during 120 min stabilization time. This shows that the tensile modulus values have increased, with an upward tendency of the samples stabilized between 15 and 30 min, followed by a gradual but steady decrease.

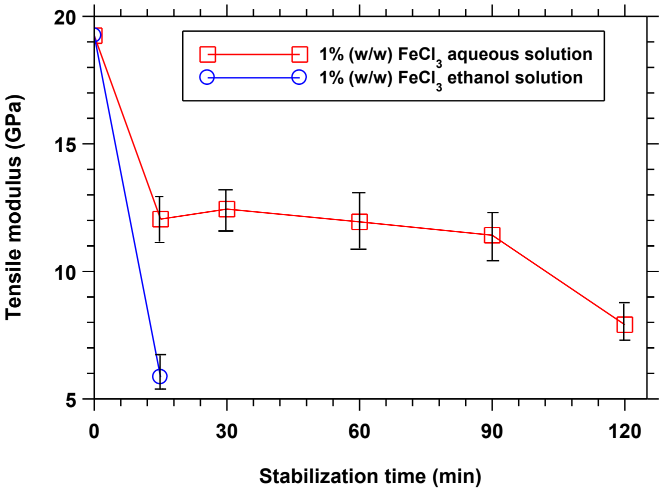


Fig. 10. Evaluation of the tensile modulus (GPa) of untreated and thermally stabilized PA6 fibers as a function of stabilization time (min) (Untreated, 15, 30, 60, 90, 120 min)

3.2. Evaluation of Fiber Characterizations (FT-IR and TGA analyzes)

Thermal analysis is a critical step in the assessment to understand the structure and properties. Given the experimental results of polymer PA6, it was not included in the fiber characterization results as the stabilization time of 15 min was not at the desired level. The experimental results of stabilized PA6 fibers impregnated in 1% $FeCl_3$ aqueous solution were found to be better than those stabilized PA6 fibers impregnated with 1% $FeCl_3$ ethanol solution. As a result, water-based results were selected for detailed fiber characterization.

3.2.1. Evaluation of FT-IR Spectroscopy Results

Infra-red spectra were collected using a Perkin Elmer® Spectrum 400 FT-IR spectrometer using a single GladiATR® diamond-reflecting ATR fixture.

Table 5. Untreated PA6 infrared spectrum band assignments [47-52]

Band position, cm^{-1}	**Band Assignment**
3450 (sh)	'Free' N-H stretching [47]
3270 (s)	Hydrogen bonded N-H stretching [47]
3190 (sh)	N-H stretch + amide (I + II) overtone [47]
3070 (m)	aliphatic C-H stretching [47]
2922 (s)	CH_2 asymmetric stretching [47]
2856 (s)	CH_2 symmetric stretching [47]
1705 (w)	Carbonyl (C=O) stretching [47]
1630 (s)	α-phase, Amide I (mainly C=O stretching) [47]
1528 (s)	α-phase, Amide II, N-H in-plane bending+C-N stretch+C-C stretching [47]
1435 (m)	CH_2 deformation (amorphous) [48]
1370 (m)	α-phase, Amide III + CH_2 (wagging) [51]
1316 (m)	γ-phase [51]
1236 (w)	γ-phase, CH_2 wagging/twisting [49,50]
1200 (m)	α-phase, Amide III + CH2 (wagging) [52]
1170 (m)	CO-NH skeletal motion (amorphous) [48,49,50]
1124 (m)	Amorphous [9] (internal standard)
973 (m)	γ-phase, Amide (CO-NH) [52]
930 (m)	α-phase, Amide (NHCO) [52]
730 (w)	Amide V mode and CH_2 rocking [47,48] (internal standard)

In this work, the 3750-900 cm^{-1} range has been used at a characteristic resolution of 2 cm^{-1}. Table 5 illustrates the assignment of infrared bands in the 3450-730 cm^{-1} area of the IR spectrum of the PA6 Polymer reported in the literature. The FT-IR spectroscopic results were carefully examined to observe the trend of chemical changes in the TOS. The untreated and oxidized PA6 multifilament infrared bands in area 3750-2450 cm^{-1} are shown in Fig. 11 for various TOS temperatures. The spectrum in Fig. 11 generally contains vibrations belonging to the methylene (CH_2) group and the NH- group in the region of wave number 3750-2450 cm^{-1}. During the stabilization times, the intensity of CH_2 bands located at 2922 and 2856 cm^{-1} gradually decreased rather than completely disappeared, as shown in Fig 11. The N-H peaks were declined gradually at 3270 cm^{-1} during stabilization reactions. The CH_2 and N-H vibration bandwidths were noted to extend by increasing the stabilization period. The IR peak at the wavenumber of 3270 cm^{-1} belongs to the hydrogen-bonded N-H stretch. It was observed that the positions of the amide I and II bands did not change much in the early stages of stabilization (Fig. 11).

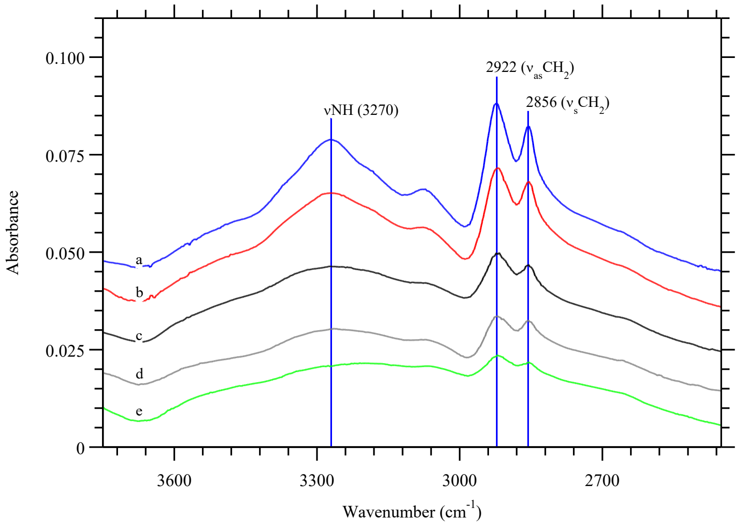


Fig. 11. FT-IR spectra of untreated (a) and 1% $FeCl_3$ aqueous solution impregnated thermally stabilized PA6 multifilament fibers as a function of stabilization time in the 3750-2450 cm^{-1} region (b) 30 min; (c) 60 min; (d) 90 min; (e) 120 min

The IR spectrum from 1825-900 cm^{-1} is assigned mainly to the amide (N-H) bands presented in Fig. 12. The vibrations at 1825-900 cm^{-1} accredited for the C=O and N-H stretch bands are based intensely on the interactions of the H bonds in the PA6 structure in Fig. 12. The intensity of the hydrogen-bond N-H band of the sample, which was stabilized at 245°C for 120 min, indicates that the H-bonds from the amide groups of polymer structure have entirely disappeared. This also confirms the total participation of hydrogen-related N-H groups in complexation with $FeCl_3$ salt.

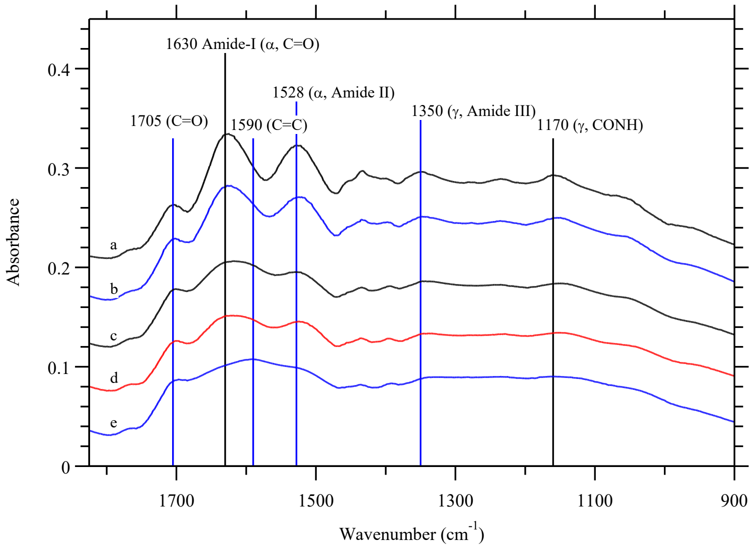


Fig. 12. FT-IR spectra of untreated (a) and 1% $FeCl_3$ aqueous solution impregnated thermally stabilized PA6 multifilament fibers of stabilization time in the 1825-900 cm^{-1} region (b) 30 min; (c) 60 min; (d) 90 min; (e) 120 min

As a result of the initiation of the de-crystallization reactions formed by incorporating ferric ions into the PA6 structure, most bands' intensities disappeared when the stabilization time of 120 minutes was reached. Based on the IR analysis, the results indicated that the incorporation of $FeCl_3$ with PA6 fibers stimulated the dehydration and dehydrogenation process.

3.2.2. Evaluation of Thermal Thermogravimetric (TGA) Analysis

TGA is one of the commonly accepted methods for investigating the thermal properties of polymeric materials. TGA results show many steps of thermal degradation, material weight loss at all stages, retention temperature, degree of degradation, and nature of degradation. The Perkin Elmer Diamond (TGA) thermogravimetric analysis system was used to derive thermograms from the untreated and thermally stabilized samples. Measurements were carried out in a nitrogen (N_2) atmosphere. Samples weight used for TGA contained 5-6 mg of PA6 fiber. The measurements began at room temperature (25°C) and were went up to 1000°C at a heating rate of 10°C/min.

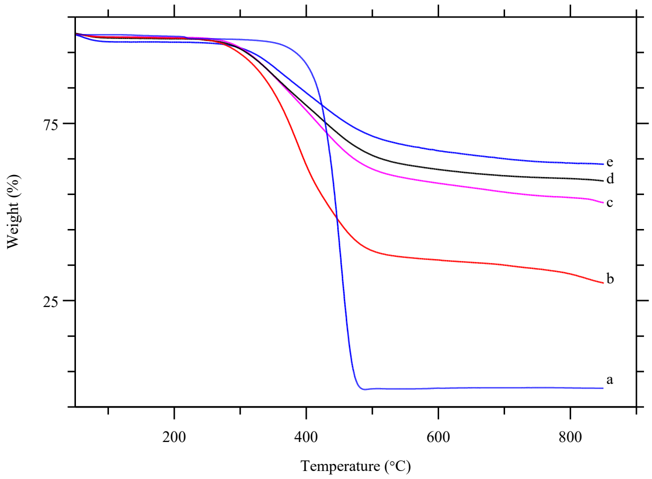


Fig. 13. TGA thermograms varying depending on the stabilization time of the stabilization samples: (a) untreated PA6; 1% $FeCl_3$ aqueous solution impregnated thermally stabilized PA6 multifilament fibers (b) 245°C 30 min; (c) 245°C 60 min; (d) 245°C 90 min; (e) 245°C 120 min

Fig. 13 shows the thermogravimetric curves of stabilized and untreated PA6 fibers. As shown in Fig. 13, mass losses are rapidly reduced as the temperature of the heat treatment increases. Untreated and stabilized PA6 fibers were observed to be stable at temperatures between 50ºC and 300ºC, and in this region, there was no mass loss. From this point, the rapid rate of degradation can reach about 490°C.

These results demonstrated that chemical pre-treatment and heat treatments effectively reduce mass loss. The TGA thermograms also showed that the carbon yield increased with increasing thermal processing temperatures.

Table 6. Comparison of carbon yields of untreated and stabilized at 245°C PA6 fibers impregnated in 1 % $FeCl_3$ aqueous solution: (a) 500°C and (b) 1000°C

Stabilization Time (min)	**Carbon yield (%) at 500°C**	**Carbon yield (%) at 1000°C**
0	3	2
30	39	27
60	62	44
90	66	50
120	72	58

The TGA thermograms presented in Table 6 show an increase in carbon yield as the stabilization time increases, indicating a decrease in mass loss caused by the gradual aromatization process. It is observed that the sample, which has been heat-treated at 245°C for 120 min, has the best carbon yield. For the 120 min stabilization time, thermally stabilized PA6 fibers, weight loss becomes 72% at 500°C and 58% at 1000°C. A comparison of the carbon efficiency for the untreated and 1% ferric chloride aqueous solution-impregnated and stabilized PA6 fibers at temperatures of 500 and 1000°C is presented in Table 6. When the carbon yield for the impregnated and thermally stabilized sample was examined, the carbon yield was found to be higher for the thermally stabilized samples than the untreated sample. Analysis of the TGA thermograms shows that due to oxidation-based cross-linking and aromatization reactions, the thermally stabilized PA6 obtains higher thermal stability. The results obtained here illustrate that the carbon yield value increases with the rise of stabilization time. This is the intermolecular cross-linking reactions that occur thanks to the active role played by the (Fe^{3+}) ions. These results show that; ferric chloride treatment provides effective stabilization, reduces mass losses, and increases carbon yield.

4. CONCLUSIONS

In this study, two-step atmospheric air-based stabilization was used for the thermal stabilization of untreated PA6 fibers. The first stage involved oxidative stabilization in the air at 170°C in the presence of ferric chloride pre-treatment. The second stage included thermal stabilization at 250°C. The impact of ferric chloride on PA6 multifilament during the thermal treatment process was examined using volume density, mechanical properties, FT-IR, TGA measurements. Physical changes were noted in terms of fiber diameter loss and increased density values with significant color changes. Experimental results show that the pre-treatment in 1% ferric chloride aqueous solution optimizes the oxidation time and aids in the rapid development of the cyclization structure. With the increase of stabilization time, the results of FT-IR showed more rapid and simultaneous cycling and dehydrogenation reactions with the help of oxygen consumption. Based on the results obtained, it is possible to see that aromatization reactions occur due to the development of (C=C) bonds resulting in aromatic structures. At lower temperatures, cross-linking and dehydration reactions have been enhanced by ferric chloride incorporation. The experimental results indicate a direct relationship between oxygen level and density. Increasing density values resulted in increased oxygen content. The obtained outcomes from the IR spectroscopy revealed a steady loss of crystallinity due to the breakage of H-bonds by the increase of the TOS period. TGA result suggests that the sample, which has been heat-treated at 245°C for 120 min, has the highest carbon yield. The carbon yield efficiency at 1000°C is about 58%, the highest value obtainable for the stabilized PA6 sample. The method of sample preparation has played an essential role in forming ferric ion coordination links with PA6 polymer chains. The integration of ferric chloride to PA6 molecular structure during the carbon fiber manufacture process is shown to speed up the stabilization reactions, which is ultimately expected to lower the total processing budget for the final carbon fiber production.

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Conflicts of Interest

There is no conflict of interest among the authors.

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