



Chemically Enhanced Wet-Spinning Process to Accelerate Thermal Stabilization of Polyacrylonitrile Fibers

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In this study, a fast and inexpensive approach is introduced to assist stabilization of polyacrylonitrile (PAN) fibers by adding ammonium iron(II) sulfate in coagulation bath. Effects of chemical treatment on stabilization process and structural evolution of fibers are studied using calorimetric, infrared, and X-ray techniques. A stepwise infrared study confirms the assisted cyclization reaction, and an X-ray analysis reveals a significant improvement in crystallinity and orientation of polymer chains which lead to an increase in tensile strength and modulus of PAN fibers. Differential scanning calorimetry results show 13 °C reductions in peak temperature of the stabilization reaction which means a sign of chemical activation at lower temperature by adding sulfate ions. Quantification of IR spectra shows a 7% increase in extent of reaction of chemically treated fibers and higher degree of conjugation compared with untreated and post-treated fibers. Finally, mechanical properties of chemically treated fibers are improved due to an increase in size and orientation of polymer chains after chemical treatment in the coagulation bath. Compared to control and post-treated PAN fibers, thermochemical properties of presented fibers are improved due to chemically assisted stabilization, and as a consequence, energy consumption of the stabilization step will be reduced by a simple and facile treatment.

1. Introduction

Carbonaceous materials and especially carbon fiber is one of the strongest and lightest materials known to date and its application is growing constantly in automotive and aerospace industries. Various precursor fibers can be converted into carbon fiber, however, polyacrylonitrile (PAN) is currently known as the main precursor of carbon fibers.^[1–4]

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Wet-spun PAN fiber is currently the precursor of more than 90% of global capacity of carbon fiber production.^[1] In this method, polymer powder is dissolved in a solvent and extruded into a coagulation bath containing a nonsolvent liquid to form the nascent fiber. In the coagulation bath, solvent leaves the polymeric dope and nonsolvent part diffuses through the polymer. Then, the excess amount of solvent is washed and the fiber is rinsed, stretched, and dried in baths and hot rollers.^[1,5–7] Several parameters such as copolymer structure, wet-spinning solvent, dope solid content, temperature of dope and coagulation bath, solvent/nonsolvent ratio of coagulation bath, jet stretch, and steam drawing ratio affect physical and thermochemical properties of precursor fibers.^[5,6,8–12]

To process carbon fiber, PAN precursor fibers are stabilized in air at low temperature and carbonized in nitrogen atmosphere at high temperature. While a crucial step in production of carbon fiber, stabilization is known to be a slow and

energy-consuming process.^[13–16] Conversion of PAN precursor to carbon fibers includes two main thermal treatment steps: (I) thermal stabilization in air atmosphere and (II) carbonization at high temperature in nitrogen/argon atmosphere.^[17,18] Stabilization step is a slow and energy-consuming process which uses about 65% of total required energy of conversion of PAN to carbon fibers and therefore significantly influences the cost of carbon fiber.^[14,15,19,20]

In previous studies,^[21–28] post-spinning of PAN fibers in presence of chemicals such as potassium permanganate, benzoic acid,^[29] succinic acid,^[22] zinc chloride, dimethylformamide (DMF),^[24] and acetic acid^[30] have been reported in order to achieve a higher mechanical performance in addition to the lower stabilization temperature. Despite all advantages of post-spinning treatments in increasing mechanical strength and Young's modulus of fibers, insufficient and nonuniform radial diffusion of chemicals into fibers still remains as a challenge.^[22,30] This is due to the slow diffusion of chemicals into the solidified fiber after its formation which consequently results in some reduction in mechanical properties of precursor and carbon fibers.^[22,30]

In this study, a new approach will be introduced to reduce energy consumption of stabilization reaction. The new treatment technique is derived based on the following mass transfer

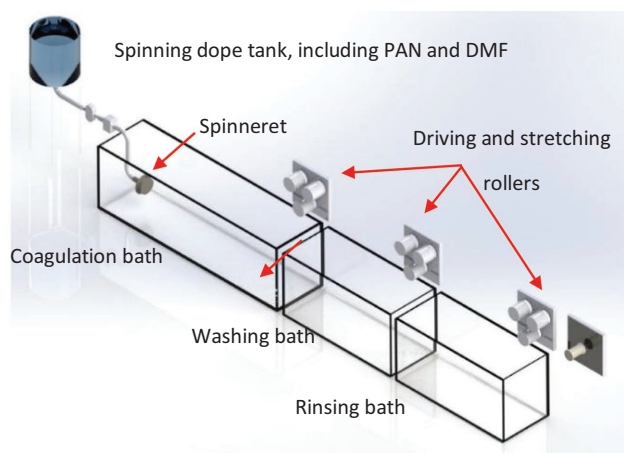


Figure 1. Schematic design of wet-spinning setup for preparing precursor fibers.

basic. Since in the coagulation bath the nonsolvent part diffuses into the fiber, a possible approach to achieve the uniform radial distribution is to dissolve a water-soluble chemical in the coagulation bath and use the nonsolvent liquid (water) as a chemical agent carrier to increase the radial homogeneity of dispersion.

As such, herein we report on using the ammonium iron(II) sulfate, $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$ which is a water-soluble salt in coagulation bath to chemically treat PAN fibres. Further reasons to use this salt is that sulfate ions act as a plasticiser, increasing the fibres stretchability and lead to a higher degree of orientation in resulting fibers. Moreover, sulfate ions can act as a cyclisation catalyst and decrease peak temperature of stabilization reaction.^[31,32] Additionally, iron(II) acts as a catalyst for cross-coupling reactions of polymeric chains including $[\text{C}-\text{H}]$ backbone and can increase the graphitic content of carbon fiber structure.^[33–35]

In this study, PAN/DMF dope was extruded into the coagulation bath of aqueous solution of ammonium iron(II) sulfate prior to further rinsing and stretching of fibers. Several analysis techniques are employed to compare the effects of chemical treatment on initiation temperature of stabilization reaction. Moreover, evolution of chemical structure of fiber during stabilization was investigated to compare effect of combined coagulation-chemical treatment method against post-treated and untreated reference sample. To the best of our knowledge, this is the first time that the ammonium iron(II) sulfate has been used as a catalyst in the coagulation bath to modify physical and chemical properties of PAN fibers.

2. Experimental Section

2.1. Wet-Spinning of PAN Fibers

PAN homopolymer ($M_w \approx 150\,000$), ammonium iron(II) sulfate, and DMF were purchased from Sigma-Aldrich, Ajax Chemical, and Chem-supply, respectively, and used as received. In order to spin fiber, polymer dope containing 18 wt% of PAN in DMF was spun through a special designed spinneret, containing 200 holes in which diameter of each hole is 50 μm .

Table 1. Wet-spinning setup and experiments conditions.

Parameter	Value or range
Spinneret specification	200 holes \times 50 μm diameter
Dope concentration	18 wt%
Ionic complex concentration in coagulation bath	20 g L^{-1}
Coagulation bath temperature	35 $^\circ\text{C}$
Coagulation bath pH	3.0
Washing bath temperature	Ambient ($\approx 20\,^\circ\text{C}$)
Stretching bath temperature	80 $^\circ\text{C}$
Drying temperature	90 $^\circ\text{C}$

Figure 1 shows the schematic of wet-spinning setup that was designed and built to prepare precursor fibers.

Table 1 includes details of the wet-spinning setup as well as the experimental conditions for wet-spinning experiments.

In order to study and compare the effect of chemical treatments on the physical and chemical properties of wet-spun fibers, three sets of samples as described in **Table 2** were prepared.

Dried precursor fibers were collected on winder for further analysis. To investigate effect of chemical treatment on evolution of chemical structure of precursor fibers, all samples were stabilized isothermally at 240 $^\circ\text{C}$ in air atmosphere for 10, 15, 30, 60, and 90 min and evolution of their chemical structure was monitored by Fourier transform infrared (FTIR) spectroscopy technique.

2.2. Characterization Methods

Tracking iron and sulfur ions on cross section of fibers was carried on by an energy-dispersive spectroscopy (EDS) technique on transmission electron microscope (TEM) instrument which had combined with a scanning transmission electron microscopy (STEM) method. Ultrathin cross-section samples were prepared by Leica UC7 ultramicrotome instrument and placed on lacey formvar TEM grids for TEM analysis.

Evolution of chemical structure was investigated using a macro-ATR measurement on PAN precursor and partially stabilized fibers by a Bruker LUMOS instrument. Selected FTIR spectra ranges were deconvoluted based on Gauss distribution by Origin software. In addition, degree of stabilization at each step (described as extent of reaction (EOR)) was calculated using Equation (1)^[36]

Table 2. Wet-spun samples and their description.

Sample	Coagulation bath composition	Post-spinning bath composition	stretching
Control	Water	Water	1.3 times
CT	Water/ammonium iron(II) sulfate (20 g L^{-1})	Water	1.3 times
PT	Water	Water/ammonium iron(II) sulfate (20 g L^{-1})	1.3 times

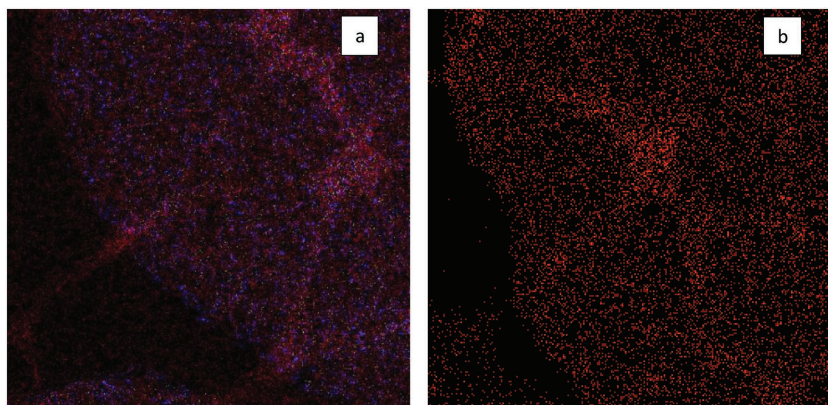


Figure 2. EDS elemental maps of a) CT precursor fiber and b) PT precursor fibers; red color represents carbon atoms, blue for sulfur, and yellow dots are for iron atoms.

$$\text{EOR (\%)} = \frac{0.29 \text{ Abs}_{\text{C=N}}}{\text{Abs}_{\text{C=N}} + 0.29 \text{ Abs}_{\text{C=N}}} \quad (1)$$

Differential scanning calorimetry technique (DSC Q-200) was carried out to monitor change of onset and peak temperatures of precursor samples in their thermal treatment steps. These two properties include important data to show the temperature range of stabilization process.

Mechanical properties of fibers were measured based on ASTM C-1557 14 using a “FAVIMAT+ AIRobot2.” A deeper investigation on physical properties of fibers was carried out by a wide angle X-ray scattering (WAXS) on precursor and stabilized fibers in Australian synchrotron center located in Melbourne, Australia. WAXS results revealed effect of processing condition on crystallites sizes and orientation of wet-spun PAN fibers. Crystallite size and interlayer spacing were calculated using Bragg’s and Scherrer equations, respectively, by considering 0.89 for the shape factor (*K*).^[6,12]

3. Results and Discussion

3.1. Radial Diffusion in the Coagulation Bath

Figure 2 presents EDS elemental maps of carbon, sulfur, and iron atoms on ultrathin cross section of wet-spun PAN fibers. As it is shown in **Figure 2a**, presence of blue and yellow dots shows diffusion of iron and sulfur atoms into the body of fiber for CT fiber samples. In contrast, collected elemental map for cross section of post-spinning treated (PT) fiber shows presence of only carbon atoms.

As a result, amount of diffused ammonium iron(II) sulfate from post-spinning bath to the fiber is less than to be traced using EDS technique and this chemical

treatment method is not as effective as chemical treatment in the coagulation bath. As it was mentioned before, because of the counter-current diffusion mechanism in the coagulation bath, a higher amount of radial diffusion was expected in a combined coagulation-chemical treatment process condition rather than a post-spinning treatment.

3.2. Effect of Chemical Treatment on the Reaction Temperature

DSC analysis was used to study the effect of chemical treatment in coagulation and post-spinning bath on the energy consumption of stabilization reaction. Three precursor fiber samples were analyzed and their thermochemical properties were compared. The stabilization reaction is considered to occur according to the mechanism presented in **Figure 3**.^[7,13,37–41] A study by Liu et al.^[42] investigated presence of oxygen during stabilization of atactic-PAN polymer and showed higher rate of chain scission was found when the polymer was stabilized in a nitrogen atmosphere. Recently Liu et al. showed the different mechanism of stabilization in air and vacuum atmosphere using ¹³C NMR study.^[41] As it is shown in their study, stabilization in air resulted in a higher aromatization that leads a higher degree of crosslinking in the stabilized fibers. However, removing air from the oven resulted

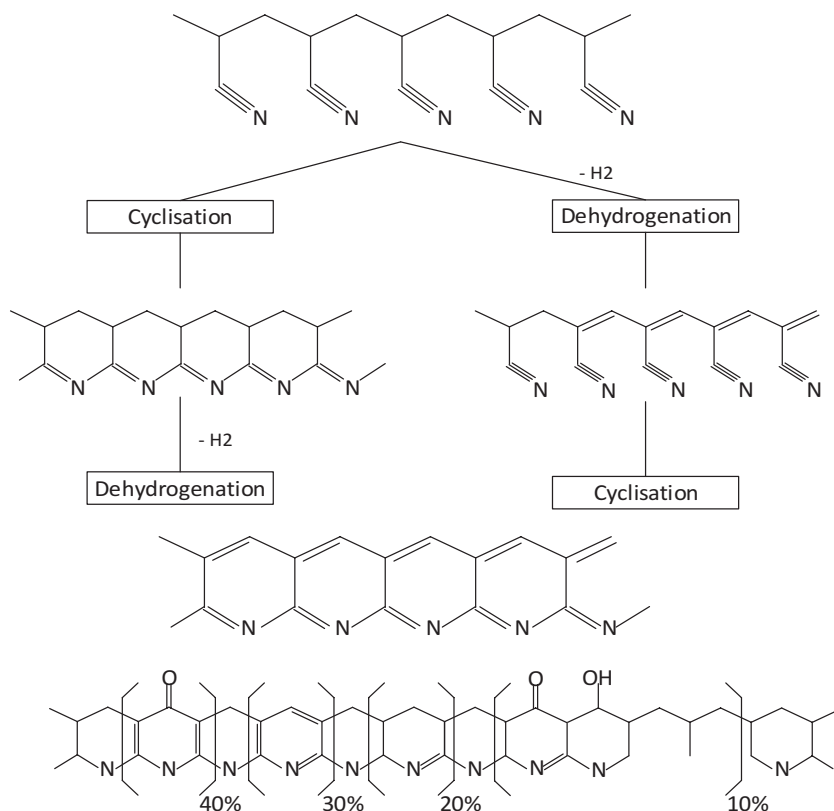


Figure 3. Proposed mechanism for stabilization reaction of PAN.

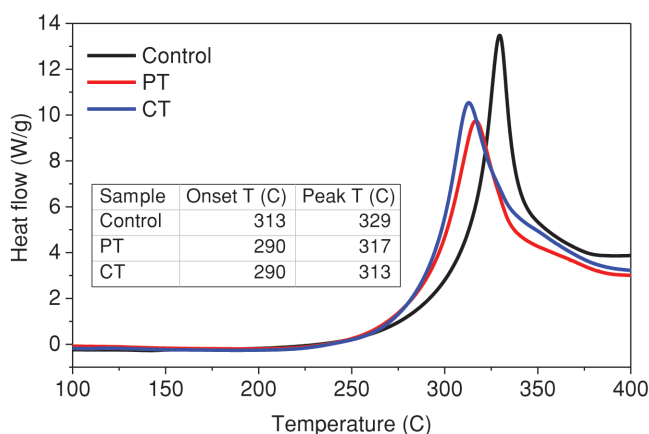


Figure 4. DSC results of control, PT and CT precursors; heating rate $10\text{ }^{\circ}\text{C min}^{-1}$ in air atmosphere.

in a higher chain scission which is known as a defect in stabilized fiber.

Effect of different heating rate on energy consumption of stabilization reactions has been previously investigated by researchers^[40] and a simulation of the stabilization oven was also represented to show the important parameters on stabilization and effect of them on properties of stabilized and carbonized fibers. Then, a constant heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ was selected and samples were heated up to $450\text{ }^{\circ}\text{C}$ in air atmosphere. **Figure 4** shows DSC results for control, PT and coagulation-treated (CT) samples and as it reveals, chemical treatment of PAN by ammonium iron(II) sulfate significantly reduced the onset and peak temperature of both chemically treated samples.

Results show a reduction in onset and peak temperature of chemically treated samples compared to untreated PAN fiber. There is a $23\text{ }^{\circ}\text{C}$ reduction in onset temperature and more than $12\text{ }^{\circ}\text{C}$ in peak temperature after chemical treatment which indicates a change in thermochemical behavior of PAN precursor. This means that the stabilization process requires a lower temperature to start and that a notable amount of energy is saved by conducting stabilization at lower temperature.

Since, the stabilization of PAN is an exothermic reaction, releasing more heat at the same onset and peak temperature shows a higher degree of completion of reaction. Analyses of released energy showed 1960 J g^{-1} exothermic energy for untreated PAN fibers which can be used as the reference value. PT and CT fibers released 2015 and 2308 J g^{-1} energy during the same test condition which shows a further degree of completion of stabilization is achieved by chemical treatment. In other words, chemical treatment in the coagulation bath assisted the stabilization reaction to be terminated by releasing more heat of reaction at the lower temperature.

The reason behind this thermochemical change is that the sulfate ions act as a catalyst in cyclisation step and according to the previous studies this can enhance the degree of stabilization by the mechanism illustrated in **Figure 5**.^[7,37–39] Herein, sulfate ions act as a negative charge ion same as MnO_4^- ions^[29] and attract to $[-\text{C}\equiv\text{N}]$ bond and weaken it. Moreover, presence of ammonium ions in the coagulation bath leads to generation

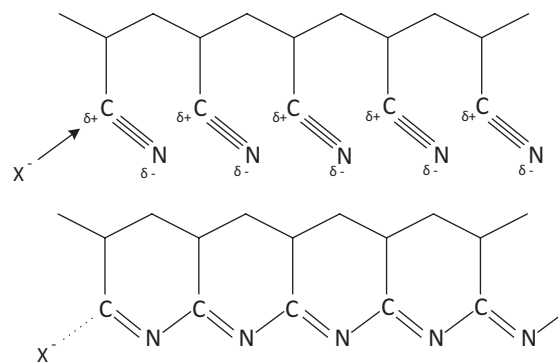


Figure 5. Proposed mechanism for the cyclisation reaction using sulfate ions.

of $[\text{OH}^-]$ group which accelerate the cyclisation reaction by the base-induced cyclisation.^[21]

Regarding the proposed mechanism, presence of higher amount of ammonium iron(II) sulfate as a catalyst can stimulate the reaction to be initiated and terminated at a lower temperature. DSC results revealed $12\text{ }^{\circ}\text{C}$ reduction in peak temperature of PT sample compared to $16\text{ }^{\circ}\text{C}$ reduction for CT fibers which is due to higher catalyst uptake in the combined coagulation-chemical treatment process.

3.3. FTIR Study of Stabilization Reactions

In order to investigate effects of chemical treatment on evolution of chemical structure during stabilization, FTIR spectroscopy was conducted on partially stabilized CT and control fibers. The main infrared absorption bands for PAN polymer are listed in **Table 3**.

Fiber samples were stabilized isothermally at $240\text{ }^{\circ}\text{C}$ in air atmosphere for 10, 15, 30, 45, 60, and 90 min and at each stage, evolution of formation of new chemical bonds and their chemical structure were monitored. **Figure 6** presents gradual evolution of chemical structure of control and CT-PAN fibers at different time-steps in air atmosphere at $240\text{ }^{\circ}\text{C}$.

Table 3. Assignment of polyacrylonitrile IR absorption band.^[13,14,43]

Wavenumber [cm^{-1}]	Functional group	References
2939 (medium)	$\nu_s-\text{C}-\text{H}$ in CH_2	[44]
2243 (strong)	$\nu_s-\text{C}\equiv\text{N}$	[44]
2210 (shoulder)	Conjugated nitriles	[45,46]
2190 (shoulder)	β -Amino nitriles	[47]
1718 (shoulder)	$\nu_s-\text{C}=\text{O}$	[44]
1660 (shoulder)	$\nu_s-\text{C}=\text{C}-$	[44]
1595	$\nu_s-\text{C}=\text{N}-$	[47]
1454	$\delta-\text{C}-\text{H}$ in CH_2	[44]
1250	$\nu_s-\text{C}-\text{C}-$ and $\nu_s-\text{C}-\text{N}-$	[48]
1045	$\nu_s\text{ S}=\text{O}$	[49]
810	$\nu_s\text{ C}-\text{H}$ in $-\text{C}=\text{C}-\text{H}$	[49]

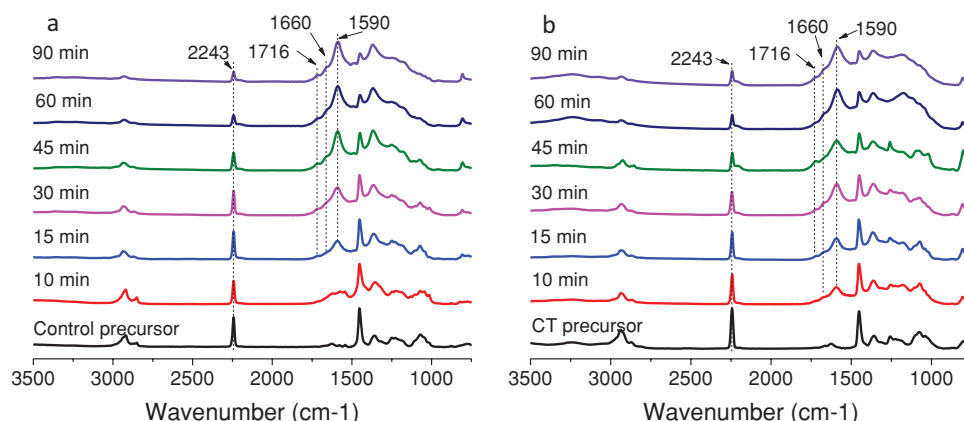


Figure 6. FTIR spectra of wet-spun precursor partially stabilized a) control and b) chemically treated fibers for 10, 15, 30, 45, 60, and 90 min at 240 °C.

The main peak of cyclisation which is located at $\approx 1590\text{ cm}^{-1}$ has appeared after 15 min for control and after 10 min in CT fibers. After 15 min $[-C=N-]$ peak at 1595 cm^{-1} becomes stronger and after 30 min two shoulders at 1716 and 1660 cm^{-1} are visible for both samples. These two shoulders are the results of oxidation and dehydrogenation steps and represent $[-C=O]$ and $[-C=C-]$ bonds, respectively.^[47] As presented in Figure 6a,b, chemical treatment in the coagulation bath stimulated cyclisation reaction of CT fibers and the reaction initiated and developed faster than untreated control fibers.

EOR values clearly presented a higher degree of conversion for stabilized CT-PAN fibers and confirmed the catalytic effect of ammonium iron(II) sulfate on structural evolution of PAN fibers during the stabilization (Figure 7). At the end of stabilization trials, calculated EOR for control and CT fibers are 53.49 and 60.01, respectively. According to the proposed mechanism of sulfate and hydroxyl groups, presence of ammonium iron(II) sulfate in the coagulation bath not only accelerates the stabilization reaction but also leads to a higher extent of reaction for the final stabilized fibers.

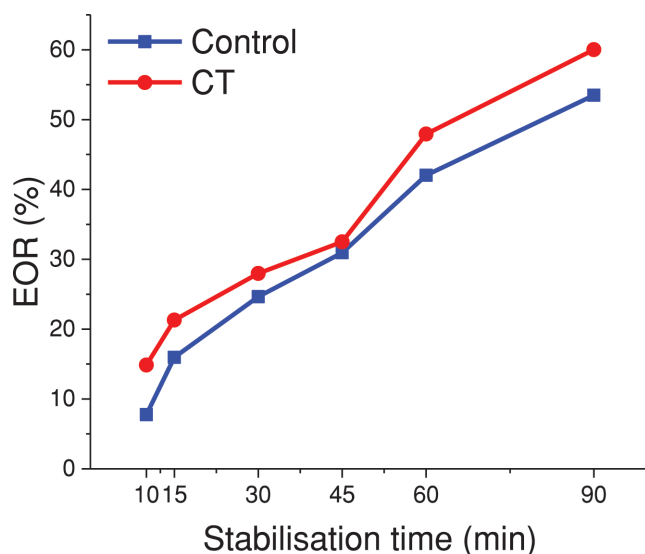


Figure 7. EOR values of stabilized control and CT fibers.

3.4. Effect of Chemical Treatment on Chains Decomposition

In order to further study and investigate effect of ammonium iron(II) sulfate on decomposition of polymer backbone in thermal stabilization process, FTIR spectra of samples between 2300 and 2100 cm^{-1} were investigated. Figure 8a,b presents the results of multiple curve fittings of control and CT-PAN samples.

There are three main peaks at 2243, 2210, and 2190 cm^{-1} that correspond to $[-C\equiv N]$, conjugated nitrile, and β -amino nitrile groups, respectively.^[13] These three peaks can be used to predict the amount of unreacted PAN (2243 cm^{-1}), ladder structure formation (around 2220 cm^{-1}), and chain scission (2190 cm^{-1}). Based on the calculations, amount of conjugated nitrile in CT fibers after 90 min stabilization is 36.34% which is 13% higher than that of stabilized control fibers. Similarly, a 3% reduction in chain scission for stabilized CT fibers was obtained.

The stepwise FTIR study confirmed when ammonium iron(II) sulfate is added into the coagulation bath, a higher degree of completion is achieved. This rapid development of structure allows reaction to be completed faster which in turn saves time and energy during thermal stabilization.

3.5. Effect of Chemical Treatment on Physical Properties

X-ray analysis was conducted to investigate effect on chemical treatment on crystalline structure of PAN fibers. Figure 9 presents X-ray patterns of PAN powder, control, **CT and PT samples. Polyacrylonitrile has two diffraction peaks at $2\theta = 16.9^\circ$ and 29.5° , which are corresponding to (1 0 0) and (1 1 0) planes of a hexagonal crystal structure, respectively.^[50–52]

As expected due to tension applied on fibers during spinning process, the amorphous region for PAN powder is more pronounced compared to PAN fibers. However, effect of tension on fiber samples is not to the same degree for treated and untreated fibers. To further understand this, crystallite sizes, degree of crystallinity,^[53] and Herman's orientation factor of polymer chains^[54] were calculated. Moreover, the tensile strength and Young's modulus for treated and untreated fiber samples were measured and results are presented in Table 4.

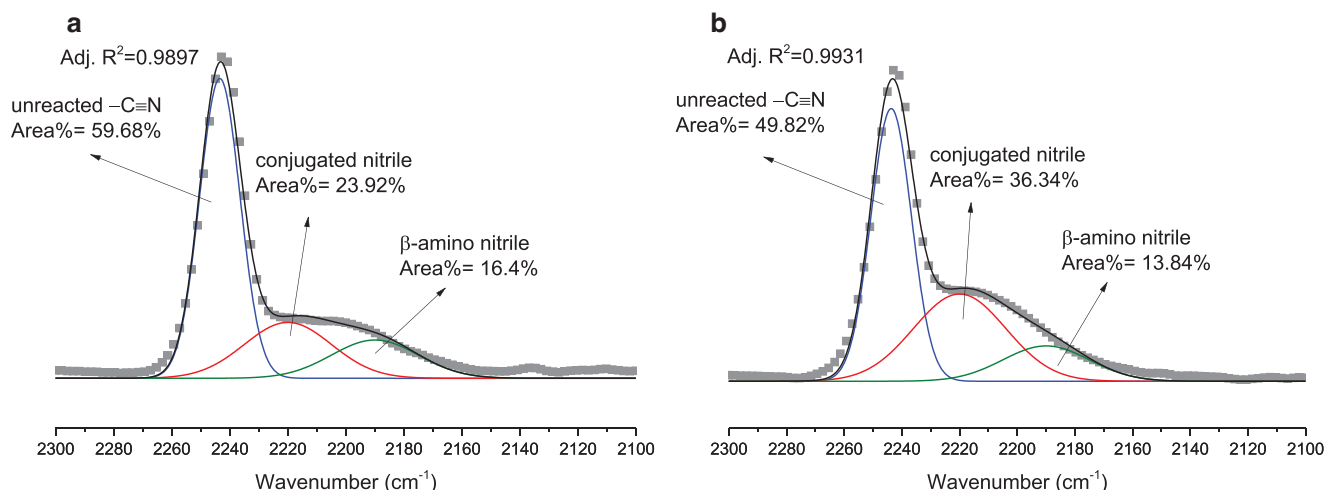


Figure 8. Multiple fit of peaks between 2300 and 2100 cm^{-1} of a) untreated and b) chemically treated fibers; both samples were stabilized at $240\text{ }^{\circ}\text{C}$ for 90 min .

The crystallite size for untreated fiber is 3.55 nm and diffusion of ammonium iron(II) sulfate into the fiber increased their sizes in post-spinning treated fibers to 4.10 nm . In comparison, presence of plasticizer (ammonium iron(II) sulfate) into the coagulation bath has had a greater impact on crystallite size and increased it from 3.55 nm for untreated samples to 7.83 nm for coagulation-treated samples. This significant increase in the crystallite size, further confirms the positive role of ammonium iron(II) sulfate in enhancing the fibers' microstructural properties. Calculating Herman's orientation factor (f_c) confirms an increase in crystallites orientation. There is a slight improvement in f_c by post-spinning treatment (i.e., from 0.32 to 0.39) and a notable increase to 0.49 when the fibers were chemically treated in the coagulation bath.

Measuring tensile strength of fiber samples revealed a 43% increase in tensile strength of fibers after post-spinning treatment, while chemical treatment in the coagulation bath led to fibers with 95% increased tensile strength. Young's modulus of post-spun treated fibers showed a slight difference with control fibers and a 48% increase in Young's modulus of CT fibers was observed compared to control fibers. This is due to the presence of ammonium iron(II) sulfate in the coagulating bath and is in good agreement with the increase in crystallinity and Herman's orientation factor obtained in X-ray study. Since ammonium iron(II) sulfate plays a plasticizer role when it is absorbed into the fibers, microstructural properties of PAN fibers are greatly improved by applying chemical treatment in the coagulation bath compared to post-spinning treatment and no chemical treatment. Larger crystallite size, higher crystallinity, and crystallites orientation in treated fibers led to enhanced mechanical performance.^[25,55,56]

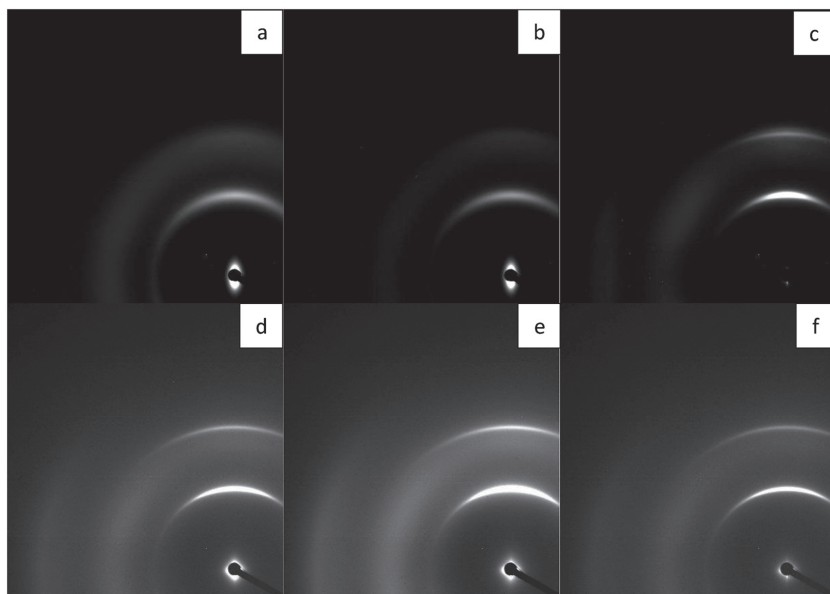


Figure 9. WAXS patterns of a) control precursor fiber, b) PT fiber, c) CT fiber, d) partially stabilized control, e) partially stabilized PT, and f) partially stabilized CT fibers.

4. Conclusion

In this study, a novel chemical approach was employed to accelerate thermal stabilization of PAN fiber and consequently, to reduce energy consumption of PAN stabilization process. Despite, most previous studies that have focused on using various copolymers which are often expensive, herein we introduced a facile chemical treatments of PAN fibers during wet-spinning to decrease reaction temperature and reduce stabilization energy consumption. DSC results revealed a $13\text{ }^{\circ}\text{C}$ decrease in peak temperature of chemically treated fibers which enables the low-temperature stabilization of PAN fibers. FTIR analysis revealed that EOR increased for chemically treated fibers compared to untreated fibers at the same reaction time and temperature. The presence of ammonium iron(II) sulfate

Table 4. Physical properties of PAN powder and fibers samples.

Sample	$L_c^a)$ [nm]	$X_c^b)$ [%]	$f_c^c)$	Diameter [μm]	Tenacity [cN dtex ⁻¹]	Young's modulus [GPa]
Powder	3.54	—	—	—	—	—
Control	3.61	59.93	0.50	11.91 \pm 1.86	1.71 \pm 0.65	6.05 \pm 0.41
PT	3.62	60.08	0.52	11.15 \pm 0.26	1.93 \pm 0.14	7.51 \pm 0.28
CT	7.63	61.91	0.65	10.73 \pm 0.22	2.03 \pm 0.35	8.96 \pm 1.65

^{a)} L_c : crystallite size; ^{b)} X_c : crystallinity; ^{c)} f_c : Herman's orientation factor.

in the coagulation bath led to 95% increase in tensile strength of treated fibers compared to untreated fibers. Improvement in mechanical performance of treated fibers can be explained by 120% increase in crystallite size and 53% in chains orientation of PAN fibers as a result of plasticizing effect of ammonium iron(II) sulfate impregnation in the coagulation bath. This study presents a simple and inexpensive approach to reduce the energy consumption and time required for stabilization of PAN fibers and paves the way for development of low-cost carbon fiber.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

carbon fibers, chemical treatment, energy consumption, polyacrylonitrile, stabilization

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