

Research Article

Analysis of Terpolymerization Systems for the Development of Carbon Fiber Precursors of PAN

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The thermal stabilization of polyacrylonitrile fibers (FPAN) is one of the most important steps in the production of carbon fibers (CFs). In this paper, new precursor polymers from PAN have been synthesized with different chemical characteristics using a solution polymerization, and FPAN was obtained using an unconventional wet spinning system in the drying and collapsing steps. The effect of different operation conditions, comonomers, and termonomers on the properties of precursor polymers, polymerization reactions, mechanical properties, structural characteristics, and stabilization of the FPAN was studied and analyzed. FTIR and optical microscopy were used to analyze structural changes of FPAN in the thermal stabilization. The impact of the chemical composition of the precursor polymers on the physicochemical characteristics of FPAN and their behavior in the thermal stabilization process were evaluated. In particular, itaconic acid monomer improved the tensile strength of the fibers from 8.07 to 16.87 cN/dtex, and the extent stabilization increased from 1.81 to 4.6. FTIR indicated that the reaction of stabilization of the terpolymer developed was initiated at a lower temperature compared to that of a commercial precursor polymer.

1. Introduction

The applications of carbon materials have continuously increased due to their properties and they include nanotechnology, porous materials, films, energy, and electronics. Polyacrylonitrile (PAN) has been recognized as one of the most important precursors of carbon fiber (CFs) [1]. More than 90% of the carbon fibers (CFs) are made from precursors based on PAN [1–6]. The quality of the precursors contributes significantly to define the properties of the resulting CFs [7]. PAN homopolymers have been rarely used as a CFs precursor due to its poor spinnability and thermal stabilization. To attend this problem, several copolymers and terpolymers of acrylonitrile were developed and used as precursors [8].

Different copolymers of PAN have been used as precursors of CFs [3, 5–7, 9] such as poly(acrylonitrile-itaconic acid) or poly(acrylonitrile-methyl acrylate) obtained by template-assisted, solution, and emulsion polymerizations. In addition, many terpolymers have been used as CFs precursors [1, 2, 4, 9] and they include poly(acrylonitrile-methyl acrylate-itaconic acid), poly(acrylonitrile-acryl amide-methyl acrylate), or poly(acrylonitrile-methacrylic acid-acryl amide). Neutral comonomers such as methyl methacrylate (MMA) or methyl acrylate (MA) can be incorporated during the polymerization for enhancing the solubility, spinnability, hydrophilicity, and drawability. Acidic comonomers (e.g., methacrylic acid (MAA), acrylic acid (AA), or itaconic acid (IA)) can be incorporated during the polymerization especially to promote the thermo-oxidative stabilization [8].

However, it is difficult to improve the stabilization and spinnability in precursors due to the different reactivities of the acidic and neutral comonomers which often results in poor performance CFs [2]. It is of great importance to continue with the study and development of new and better terpolymer systems that allow improving the physical and chemical properties of precursor, and that can lead to the reduction of processing costs of CFs.

The thermal stabilization of fibers of PAN (FPAN) is one of the steps that consumes more energy in the global process to prepare CFs [1, 9]. The chemical structures of FPAN and the stabilization conditions as the rate of air-flow, the sequence of temperature zones, tension on the fibers, heating rate, and heating atmosphere (nitrogen or air) determine the stabilization efficiency [9, 10]. The addition of comonomers during the polymerization increases the steric hindrance between the polymer chains affecting their crystallinity and orientation; hence, this defines the shrinkage of the fibers, the temperature at which the stabilization reaction occurs, and the total mass lost [9]. The chemical structures of FPAN are defined by the composition, types, and distribution of comonomers in the backbone of the PAN chains.

In the synthesis of CFs precursors by solution polymerization, the control of processing conditions is crucial to obtain the high quality of the precursors. The polymer conversion rate, average molecular weight, and the thermal stabilization of the precursors are characteristics that can be controlled by adjusting parameters such as the types of comonomers and their molecular structure [2, 11–13], the reaction medium, reaction temperature, and the concentration of the comonomers [14–18]. However, most studies only focused on one parameter and did not examine the combined effects in the polymerization process of copolymers and terpolymers over the principal objectives to produce CFs like high polymer conversion rate, high average molecular weight, and easy stabilization. Also, these studies failed to obtain the optimal conditions for solution polymerization. Herein, it is convenient to highlight that the orthogonal experimental design from the Taguchi methodology is one of the most effective tools to find the optimal process operating conditions (including those of polymerization systems) via the combination and analysis of multiple factors or variables. The Taguchi approach allows to analyze multiple factors over one or more objectives or response variables using a reduced number of experimental trials with a high accuracy level [19–22].

Therefore, this paper reports the analysis of different terpolymerization systems to develop terpolymers of PAN (TPAN) as precursors of CFs and using experimental optimization based on the Taguchi method for the total conversion of monomers, average molecular weight, and the extent of stabilization for the terpolymers obtained in solution polymerization reactions. TPAN were processed in a nonconventional wet spinning system respect to the traditional process [1, 4, 9] and were thermally stabilized. The results of this study were compared with a fiber obtained from a commercial copolymer.

TABLE 1: Variables and tested values for the experimental design of terpolymerization systems.

Variable		Level 1	Level 2
A	Temperature (°C)	50	60
B	Ratio initiator/MT ^a (wt %)	0.01	0.02
C	Ratio solvent/MT (wt %)	3	5
D	Comonomer/MT (wt %)	5	10
E	Termonomer/MT (wt %)	1	3
F	Comonomer type	VA	MA
G	Termonomer type	IA	BA
H	Reaction time (h)	1	2
I	Stirring rate (rpm)	250	350

^aMT: total monomers.

2. Materials and Methods

2.1. Materials for the Solution Terpolymerization. All chemical reagents were purchased from Aldrich, St. Louis, MO, USA, and were used as received. They included monomers, acrylonitrile (analytical grade) $\geq 99\%$ containing 35–45 ppm monomethyl ether hydroquinone as inhibitor (AN), methyl acrylate 99% (MA), vinyl acetate 99% (VA), itaconic acid (IA), and boric acid (BA), the initiator ammonium persulfate (AP) and the solvent N,N-dimethylformamide (DMF).

2.2. Test Conditions for the Synthesis and Characterization of Terpolymers. An experimental design was defined via the Taguchi approach in order to analyze the effect of some variables of the terpolymerization system on the properties of TPAN. Two levels were considered in the Taguchi experimental design for tested nine variables. Therefore, a L_{12} orthogonal array was selected for this study where each run was performed two times to ensure reproducibility. Therefore, a total of 24 data values were collected and analyzed in this study. TPAN samples were identified according to the experiment number as TPAN-1, TPAN-2, TPAN-3, ..., TPAN-12. The variables and ranges used in this experimental design are shown in Table 1. These conditions were defined based on an industrial process (i.e., a confidential process from the Mexican CYDSA industry) and the results of previous studies. AP was used as an initiator because of its high reactivity, solubility in various media, and the important results found in the researches [23–25]. The type of comonomers and termonomers and their concentrations were analyzed based on their impact on reaction yields, molecular weights, and thermal behavior [14, 24–30]. Finally, the operating conditions such as stirring rate, reaction temperature, and time were established from literature [24–27]. An analysis of variance (ANOVA) was performed using Minitab statistical software (Version17). ANOVA is a statistical method used to estimate the individual effects from all control factors on tested response variables [31, 32].

The terpolymers poly[acrylonitrile-co-(methyl acrylate)-co-(itaconic acid)] [P(AN-MA-IA)], poly[acrylonitrile-co-(methyl acrylate)-co-(boric acid)] [P(AN-MA-BA)], poly[acrylonitrile-co-(vinyl acetate)-co-(itaconic acid)] [P(AN-VA-IA)], and poly[acrylonitrile-co-(vinyl acetate)-co-(boric

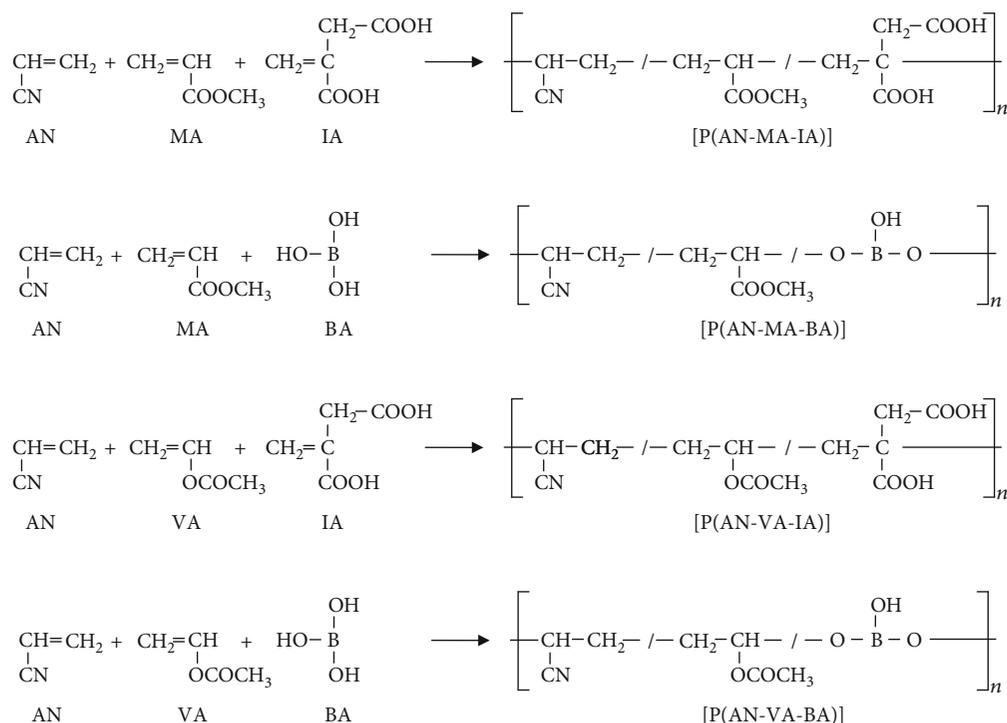


FIGURE 1: Reactions of PAN terpolymerization used in this study.

acid)] [P(AN-VA-BA)] were synthesized through a solution-free radical polymerization in air atmosphere. DMF and the monomers were added simultaneously in a 100 mL three-necked flask, which was adapted with a stirring system and a water bath to control the temperature, according to the established experimental conditions. The initiator previously dissolved in DMF was added after 10 minutes of stirring. The terpolymerizations were carried out at the experiment temperature, and, after a certain time, the reaction was stopped by adding 50 mL of deionized water. The precipitated solid TPAN was washed with 100 mL of deionized water at 80°C for several times, and it was recovered by filtration and dried at 55°C for 24 h. For illustration, the chemical reactions of terpolymerizations are shown in Figure 1. The monomers were activated by coordination with the active centers of the PA initiator. The neutral monomer (VA or MA) and acidic monomer (IA or BA) were added in the growing chain of AN caused by reactivity ratios between the monomers [33, 34].

The total conversion rate of TPAN ($Conv$) was calculated by the ratio of its dried mass to the total mass of the initial monomers. The average viscosimetric molecular weight of TPAN (\overline{M}_v) was obtained with an Oswald viscometer and calculated by the Mark-Houwink equation where $[\eta] = 0.617 \times 10^{-4} \overline{M}_v^{0.829}$ and $[\eta]$ is the intrinsic viscosity [35]. TPAN samples were finely pulverized, and 0.2 g of each TPAN was thermally treated in an oven with an air atmosphere at 220°C for 0.5 h. Structural changes of TPAN samples before and after the thermal treatment were analyzed using an FTIR Thermo Scientific Nicolet iS10 FTIR spectrometer. Samples of raw TPAN and thermally treated TPAN were finely pulverized and compacted at 23°C to obtain films with a thickness of 0.1-0.2 mm [36], which were used in the

FTIR analysis. The thermal treatment and FTIR analysis were repeated at least three times for each sample, and mean values were reported. FTIR analysis of each sample was performed using 64 scans in the range of 4000-400 cm^{-1} . The extent of stabilization was evaluated using FTIR spectra of thermally treated terpolymers according to Lambert-Beer's law and with the parameter Es [6, 8, 11], which is defined as:

$$Es = \frac{A_{1595 \text{ cm}^{-1}}}{A_{2243 \text{ cm}^{-1}}} \quad (1)$$

where $A_{2243 \text{ cm}^{-1}}$ is the absorption intensity of the nitrile groups ($-\text{C}\equiv\text{N}$), $A_{1595 \text{ cm}^{-1}}$ is the absorption intensity of groups $-\text{C}=\text{N}$ and $\text{C}=\text{C}$ in the FTIR spectra, respectively. Note that the intensity of the nitrile groups band at 2243 cm^{-1} decreases as the stabilization proceeds, while the band at 1595 cm^{-1} also increases showing the conversion of linear structures to ladder structures cyclized [9]. Figure 2 shows the cyclization reaction in poly(AN-co-IA) initiated through an ionic mechanism [8].

2.3. Wet Spinning and Characterization of Fibers. A commercial-grade acrylic polymer (PCOM) was used to prepare FPAN in a laboratory-scale wet spinning system. PCOM was provided by Grupo Textil de Aguascalientes, with a composition of AN-MA (90 wt% AN, 10 wt% MA). The spinning system was designed and manufactured in previous studies [25]. The schematic diagram of the spinning machine is shown in Figure 3. DMF was used as the solvent and deionized water as the nonsolvent. The spinning solution was prepared by dissolving PCOM in DMF at 70°C and stirred at 350 rpm for 2 h. The spinning solution was driven from the

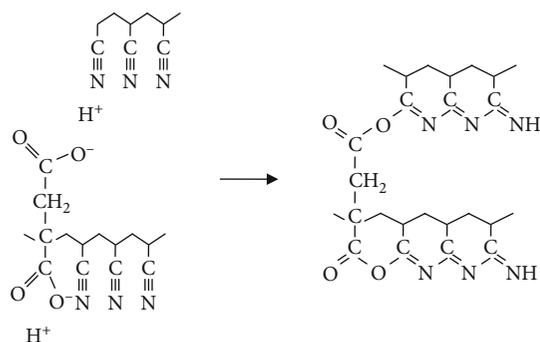


FIGURE 2: Cyclization in poly(AN-co-IA) initiated through an ionic mechanism [8].

storage column to the coagulation bath at a constant pressure. The jet was led by a drive roll to the washing bath. The formed fibers were stretched to reduce their diameter and to improve their molecular orientation. Subsequently, the fibers were passed multiple times upon a dryer plate to remove moisture and improve their strength. After that, the fibers were passed upon a second dryer plate to collapse them. Finally, the fibers were collected on a collection roll and characterized.

An optical microscope (Digital Microscope VHX 5000) was used to observe the cross-sectional morphology of FPAN. The longitudinal surface morphology of FPAN was observed using a scanning electron microscope (SEM) JEOL, JSM-5600LV. The linear density of the fibers was measured by the standard microbalance technique, and the mechanical properties were obtained from a single fiber strength tester F012 SDLATLAS. The operating conditions of spinning were defined in previous studies [25], and they are reported in Table 2. The spinning solution concentration corresponds to the mass concentration of a polymer in DMF, while the coagulation bath concentration refers to the mass concentration of DMF in deionized water. The drying steps indicate the number of times that the fibers were passed through the hot metallic surface of the dryer plate.

2.4. Stabilization of Carbon Fiber Precursor. The thermal stabilization of fibers was carried out in an oven with an air atmosphere at different times and temperatures, see Table 3. Structural changes of the fibers before and after the thermal treatment were analyzed using FTIR spectra. FTIR analysis of each sample was performed using 64 scans in the range of $4000\text{--}400\text{ cm}^{-1}$. Differential scanning calorimetry (DSC) curves of fiber samples were obtained with a TA instrument Modulated DSC 2910 under N_2 (49 mL/min).

3. Results and Discussion

3.1. Characterization of Terpolymers. As stated, the parameters Conv , \overline{M}_v , and E_s of TPAN synthesized by solution polymerization can be controlled by the concentration of the monomers, stirring rate, reaction temperature, and time of the systems of terpolymerization [12, 14–16, 28, 37]. Therefore, Table 4 shows the layout of the array L_{12} and the results of the different terpolymerizations. It is worth to mention

that the data Conv , \overline{M}_v , and E_s were the average of the two replicates of each experimental run.

The effect of tested variables of the terpolymerization systems on Conv , \overline{M}_v , and E_s of TPAN was summarized via ANOVA results, which are shown in Table 5. Note that it was used the mean ratio between the mean square value for each level of the factors over the mean square value of the error and defining a confidence level of 95% (i.e., the level of significance was 5%). Table 5 shows the values of F (Fisher distribution) and p value of each factor considering Conv , \overline{M}_v , and E_s as response variables. Comparatively, a high F -value implied a significant influence on the response variables. Table 5 shows that factors B, C, G, and H significantly affected Conv , \overline{M}_v , and E_s . Factors D and I were not relevant for any of the response variables. According to F -values, the order of the factors that affected Conv was as follows: ratio solvent C > ratio initiator B > temperature A > termonomer type G [15, 17, 29]. The ratio of solvent in the reaction medium could define the polymer conversion rate due to its high chain transfer coefficient. DMF-rich reaction medium leads to low polymerization rates [38]. The effect of the ratio initiator and temperature reactions were related to the formation of free radicals. The increase in the concentration of AP and temperature could generate higher production of active sites thus increasing the Conv -values [39, 40]. On the other hand, the concentration and polarity of the acidic termonomer affected the polymer conversion and its addition to the polymer chains due to interactions with the reaction medium. BA could have a better incorporation within the polymer chain, increasing Conv due to its lower polarity compared to IA [14, 38]. The use of short reaction times and the manipulation of other control parameters such as temperatures, initiators, type of monomers, reaction medium, and synthesis methods (solution polymerization) can lead to the development of new precursor polymers CFs with specific characteristics that compensate for low polymer conversion. Furthermore, it is possible to recycle the unreacted monomers in this type of system. It was observed that the use of a water-soluble initiator ammonium persulfate at certain operating conditions allowed to obtain polymer conversions above 40% at a short reaction time, see results of TPAN-4, TPAN-9, TPAN-11, and TPAN-12. Some solution polymerization studies with similar systems have used AIBN as the initiator and reported reaction times greater than 5 h to obtain polymer conversions above 40% [17, 19, 25, 32].

The factors that affected the \overline{M}_v in order of magnitude were ratio solvent C > termonomer type G > reaction time H > termonomer concentration E [18, 29, 30, 38]. It is well known that a higher \overline{M}_v in the precursors of PAN allows to obtain CFs with greater strength and fewer defects [7]. The effect of ratio solvent on \overline{M}_v was related to the monomer diffusion processes in the reactive medium and the high chain transfer coefficient of DMF. High concentrations of solvent lead to low molecular weights due to the high rate of completion of the reaction thus reducing the degree of polymerization and resulting in low \overline{M}_v . A low solvent concentration should increase the \overline{M}_v of the TPAN [38, 41]. The impact

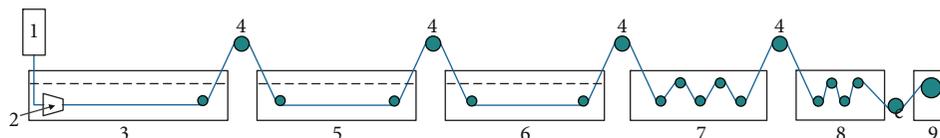


FIGURE 3: Schematic of wet spinning line. 1, storage column with a spinning solution; 2, spinnerette; 3, coagulation bath; 4, driven rollers; 5, washing bath; 6, stretching bath; 7, drying; 8, collapsing; 9, collect-rolling.

TABLE 2: Operating conditions employed in the spinning system.

Description	Value
Spinning solution concentration (wt %)	20
Coagulation bath concentration (wt %)	30
Collection speed at the end of coagulation bath (m/min)	1.5
Coagulation bath temperature (°C)	27
Washing bath temperature (°C)	40
Drying temperature (°C)	120
Steps of drying	11

TABLE 3: Conditions for the thermal stabilization of fibers.

Test	Temperature (°C)	Time (min)
1	200	20
2	220	20
3 ^a	200, 220	20, 20

^aThis test was done in two steps: in the first step, a sample of fiber was thermally treated at 200°C for 20 min. In the second step, the sample of fiber treated at 200°C was again treated at 220°C for 20 min.

of the concentration and type of termonomer on the \overline{M}_v can be mainly attributed to its molecular weight, reactivity ratio, and the interactions with the reaction medium. High molecular weight termonomers should increase the volume and molecular size of TPAN, resulting in high \overline{M}_v -values [38]. The termonomer concentration in the feed must be carefully controlled since a high concentration counteracts the growth of the chains [13]. Reaction time represents an important variable for the control of molecular weight and is directly related to the distribution of molecular weights and the diffusion processes of the monomers. In tested operating range, the shorter reaction times allowed to obtain polymers with higher \overline{M}_v -values.

Finally, the factors that impacted on the E_s were as follows: termonomer type $G >$ termonomer concentration $E >$ ratio initiator $B >$ ratio solvent C [25]. The progress of the stabilization of TPAN was a function of the initiation mechanism of the cyclization reaction of nitrile groups. It is well known that cyclization in homo-PAN is initiated through a free radical mechanism, and, in TPAN with acidic termonomers, the cyclization reaction follows an ionic mechanism [8, 13, 42]. A higher concentration of termonomer improves the E_s . As in \overline{M}_v analysis, the amount of termonomer in the feed must be carefully controlled since a high concentration leads to thermally fragile systems [29]. The influence of the ratio initiator and ratio solvent on stabilization may be related to the homogeneity of the structure of the polymer chains. Higher monomer amount and lower initiator concentration

lead to obtain polymers with low structural defects [15]. The distribution of comonomers in the polymer chain and the structural order may promote the cyclization of nitrile groups by the mobility of the comonomers adjacent to the AN, which are more active in initiating the cyclization reaction [6]. The higher solvent concentration leads to the formation of complexes due to the high chain transfer coefficient, setting the structural order of the polymeric chains [38].

TPAN samples were submitted to thermal treatment and analyzed by FTIR to observe structural changes, see Figure 4. The typical broad peak around 2243 cm^{-1} was assigned to the characteristic stretching vibration of the $\text{C}\equiv\text{N}$ group, indicating a long chain on AN monomer units in all the TPAN [8]. The assignments of other absorption bands are given as follows [4, 8, 11, 41, 43, 44]: $-\text{CH}_2$ stretching at 2939 cm^{-1} , $-\text{C}=\text{O}$ stretching at 1730 cm^{-1} , the combination of $-\text{C}=\text{N}$ and $\text{C}=\text{C}$ stretching at 1595 cm^{-1} , $-\text{CH}$ stretching at 1450 cm^{-1} , $\text{B}-\text{O}$ at 1430 cm^{-1} , combination $-\text{C}-\text{C}$ of $-\text{C}-\text{O}$ at 1230 cm^{-1} , and $-\text{B}-\text{HO}$ at 1200 cm^{-1} . All TPAN samples treated thermally showed the decrease of the band intensity at 2243 cm^{-1} of $\text{C}\equiv\text{N}$ groups, and also the increase of the bands at 1595 and 1730 cm^{-1} corresponding to groups $\text{C}=\text{C}$ and $\text{C}=\text{O}$, respectively.

The changes in the band of $\text{C}\equiv\text{N}$ groups were more remarkable for TPAN with IA than those for TPAN with BA, see Figures 4(a) and 4(b). These results confirmed that the termonomer IA significantly promoted a greater formation of cyclic structures [8, 9, 29]. According to the Lambert-Beer's law, the ratio of absorbance of the bands at 1595 and 2243 cm^{-1} was approximately proportional to the ratio of the content of residual $-\text{C}\equiv\text{N}$ groups and the formed $\text{C}=\text{C}$ and $\text{C}=\text{N}$ groups [6, 8, 11]. Since the conditions of the thermal treatment of TPAN were the same, a larger value of E_s implied that there was a greater formation of cyclic structures with the thermal treatment [6, 8, 11]. In this way, it can be observed that the values of E_s and the changes in the FTIR spectra were larger and more significant in TPAN with IA (TPAN: 1, 3, 5, 9, 10, and 11), suggesting that there was a higher concentration of $-\text{C}=\text{C}$ and $-\text{C}=\text{N}$ groups compared to TPAN with BA termonomer. The economy of a CFs production process can be promoted by optimizing the time and temperature. A polymer with a higher value of E_s indicates that it is more reactive during heat treatment. So, the structural changes can be obtained at lower temperatures and times. FTIR results and E_s were consistent; they showed that the termonomer type significantly affected the E_s of TPAN and that the termonomer IA favored it since it contained two carboxylic acid groups in its structure facilitating the cyclization reaction of the nitrile groups and initiated through an ionic mechanism [9, 45].

TABLE 4: Layout and results of L12 experimental design of the terpolymerization systems.

Test	Code	Controllable factors									Conv (%)	\overline{Mv} (g/mol)	Es
		A	B	C	D	E	F	G	H	I			
1	TPAN-1	50	0.01	3	5	1	VA	IA	1	250	17	98.14×10^4	4.0
2	TPAN-2	50	0.01	3	5	1	MA	BA	2	350	36	58.11×10^4	1.0
3	TPAN-3	50	0.01	5	10	3	VA	IA	1	350	12	51.28×10^4	4.6
4	TPAN-4	50	0.02	3	10	3	VA	BA	2	250	44	50.36×10^4	1.2
5	TPAN-5	50	0.02	5	5	3	MA	IA	2	350	31	27.43×10^4	4.3
6	TPAN-6	50	0.02	5	10	1	MA	BA	1	250	30	27.81×10^4	0.7
7	TPAN-7	60	0.01	5	10	1	VA	BA	2	350	32	48.31×10^4	1.8
8	TPAN-8	60	0.01	5	5	3	MA	BA	1	250	28	30.65×10^4	1.6
9	TPAN-9	60	0.01	3	10	3	MA	IA	2	250	41	56.53×10^4	4.7
10	TPAN-10	60	0.02	5	5	1	VA	IA	2	250	34	37.74×10^4	4.2
11	TPAN-11	60	0.02	3	10	1	MA	IA	1	350	48	87.22×10^4	1.6
12	TPAN-12	60	0.02	3	5	3	VA	BA	1	350	53	59.21×10^4	1.3

Conversion rate (*Conv*); average viscosimetric molecular weight (\overline{Mv}); and extent of stabilization (*Es*) of TPAN developed by solution terpolymerizations.

TABLE 5: ANOVA results for the experimental design used in terpolymerization systems.

Variable	<i>Conv</i>		\overline{Mv}		<i>Es</i>	
	<i>F</i> -ratio (<i>F</i>)	<i>p</i> value (<i>p</i>)	<i>F</i> -ratio (<i>F</i>)	<i>p</i> value (<i>p</i>)	<i>F</i> -ratio (<i>F</i>)	<i>p</i> value (<i>p</i>)
A	30.22	0.032	0.79	0.469	0.08	0.805
B	37.81	0.025	15.36	0.059	3.85	0.189
C	39.29	0.025	634.49	0.002	2.59	0.249
D	0.51	0.549	0.08	0.806	0.72	0.486
E	0.89	0.445	82.70	0.012	4.36	0.172
F	3.27	0.212	12.79	0.070	2.36	0.264
G	10.81	0.081	135.87	0.007	53.58	0.018
H	7.28	0.114	97.52	0.010	2.31	0.268
I	0.15	0.735	0.01	0.921	0.83	0.460

Conversion rate (*Conv*); average viscosimetric molecular weight (\overline{Mv}); and extent of stabilization (*Es*) of TPAN developed by solution terpolymerization.

The presence of BA in the FTIR spectrum should be observed at 1430 and 1198 cm^{-1} [46, 47]. However, the signals were hidden by the overlap with the bands at 1450 and 1230 cm^{-1} , which corresponded to -C-H and -C-C groups, respectively. The changes in the FTIR spectrum after heat treatment in TPAN with BA were negligible. Note that BA did not favor the cyclization reaction, and it can be observed in lower *Es*-values. BA could be acting as an electron acceptor of the adjacent atoms in the polymer chain, reducing the capacity to attack the carbon atoms in nitrile groups and transformed them into cyclic structures [47]. The effect of BA on PAN fiber stabilization has been studied, and it was found that BA can promote chain crosslinking, resulting in thermal stability, and high carbon yield after carbonization [47]. The dehydrogenation reaction reduces the concentration of -CH groups and can be observed by decreasing the bands at 1450 cm^{-1} in the FTIR spectra

[42, 48]. Interestingly, the changes in band intensity caused by the dehydrogenation reaction were most noticeable in P[AN-IA-VA], see Figure 4(a). Furthermore, the different P[AN-IA-VA] samples have high *Es*-values, indicating a more efficient stabilization process. However, this does not guarantee to obtain highly developed carbon materials after the carbonization step [42].

In the tested polymerization system, the effective incorporation of IA and other comonomers (MA and VA) in the polymerization of PAN was observed. Results from the characterization of the terpolymers and ANOVA analysis indicated that it is possible to define ideal operating conditions to develop precursors with tailored characteristics, such as the high molecular weight and low stabilization temperature, which are key parameters to the easy preparation of CFs.

In fractional experimental designs, the confirmation experiment is very important [49]. Therefore, confirmation experiments were performed for each response variable to validate the conditions to improve the *Conv*, \overline{Mv} , and *Es*. Three new tests were defined using ANOVA analysis, and three new terpolymers were synthesized. The first was made to improve the conversion rate of terpolymer (TPAN-A), the second to improve the average viscosimetric molecular weight (TPAN-B), and the third to improve the extent of stabilization (TPAN-C). The conditions of each test are shown in Table 6.

Table 6 shows that a low level of factor C increased both *Conv* and \overline{Mv} . However, the increase of \overline{Mv} can be achieved using all other factors at level 1, but it was the opposite to increase *Conv*. Also, it is suggested to use IA to increase the \overline{Mv} and *Es*, but the *Conv* is reduced. Results of the characterization of TPAN-A, TPAN-B, and TPAN-C are shown in Table 7.

Operating conditions were determined in order to obtain a new terpolymer with desirable overall characteristics based

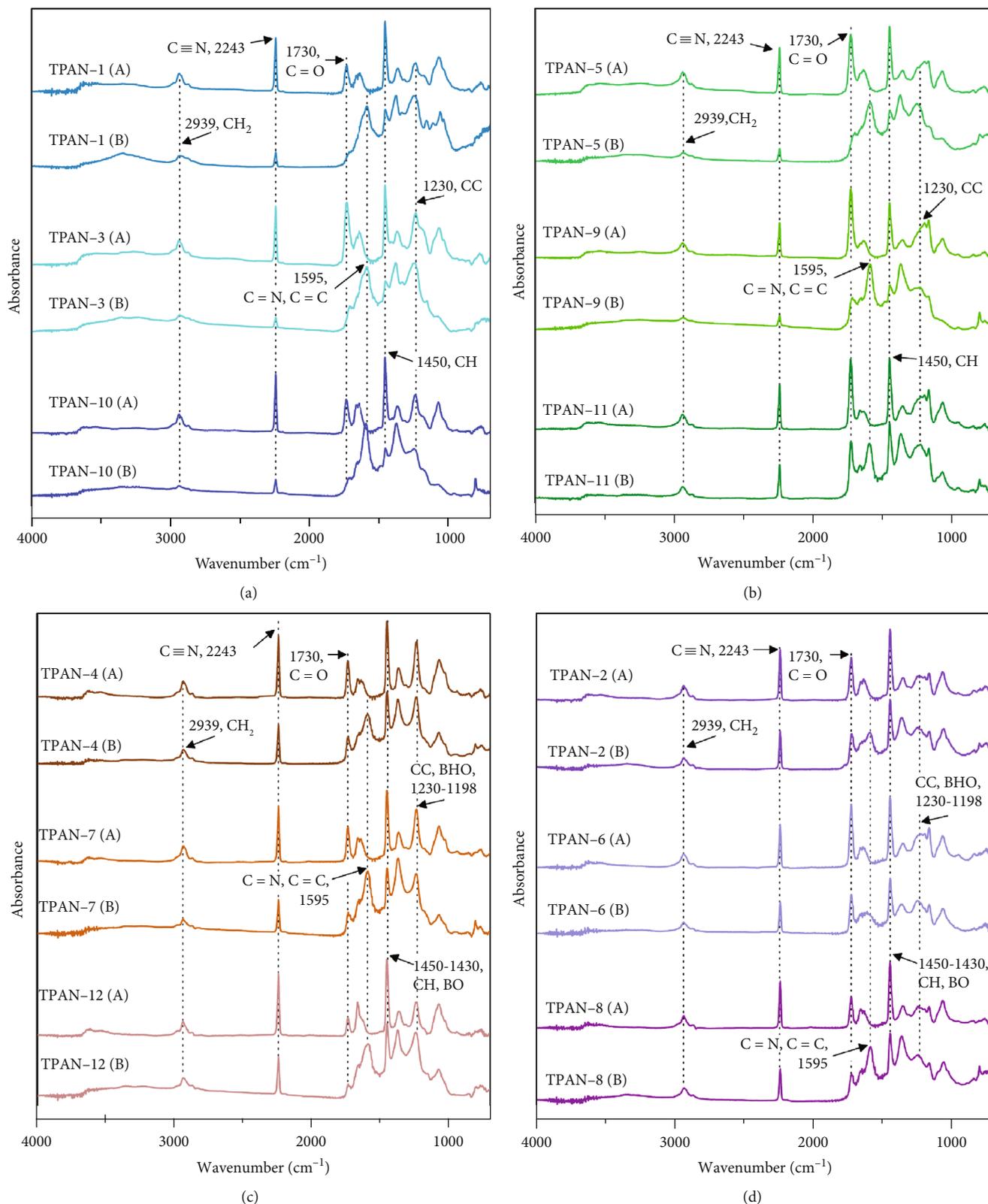


FIGURE 4: FTIR spectra of TPAN samples: (a) [P(AN-IA-VA)]; (b) [P(AN-IA-MA)]; (c) [P(AN-BA-VA)]; (d) [P(AN-BA-MA)], (A) original and (B) heated at 220°C for 0.5 h, respectively.

on previous results. The new terpolymer was defined as TPAN and the operating conditions to synthesize it and the results of its characterization are shown in Table 8.

The results of the characterization of TPAN-A, TPAN-B, TPAN-C, and TPAN-D showed very well quantitatively characteristics for the terpolymers obtained by the solution

TABLE 6: Terpolymerization conditions used to improve the conversion rate of terpolymer $Conv$, average viscosimetric molecular weight (\overline{Mv}), and extent stabilization Es .

Variable	TPAN-A		TPAN-B		TPAN-C	
	Value	Level	Value	Level	Value	Level
A	60	2	50	1	50	1
B	0.02	2	0.01	1	0.01	1
C	3	1	3	1	5	2
D	10%	2	10%	2	5%	1
E	3%	2	1%	1	3%	2
F	MA	2	VA	1	VA	1
G	BA	2	IA	1	IA	1
H	2	2	1	1	1	2
I	350	2	250	1	350	2

TABLE 7: Properties of new terpolymers of PAN.

Terpolymer	$Conv$ (%)	\overline{Mv} (g/mol)	Es
TPAN-A	55	40.95×10^4	1.6
TPAN-B	28	147.34×10^4	1.3
TPAN-C	31	108.38×10^4	5.2

Conversion rate ($Conv$); average viscosimetric molecular weight (\overline{Mv}); and extent of stabilization (Es) of TPAN developed by solution terpolymerization.

polymerization system. The first three terpolymers can be used for special applications in fibers production, where it is necessary to specifically improve one characteristic, for example, TPAN-A can be used to obtain low-cost fibers for the high productivity of the reaction, but the mechanical properties will be not with high values. The second one, TPAN-B, is an important polymer for strength fibers, and the last one TPAN-C is a polymer with high thermal reactivity. For the objective of this research, the terpolymer TPRE was the best polymer showing a good conversion for this type of polymerization at very short residence time, besides very good average molecular weight and excellent thermal reactivity. Note that these are the most important characteristics to obtain precursor fibers of CFs. The chemical composition to prepare this terpolymer was 10% MA, 1% IA, and 89% AN.

The optimal conditions obtained by the initial factorial experimental design only are valid in the range of the analyzed experimental conditions. The conclusions of the statistical analysis were applied to increase the analyzed experimental range and to improve the reaction productivity, thermal reactivity, and average molecular weight thus achieving an overall high-performance CFs precursor. For these reasons, these conclusions are valid quantitatively and statistically in a wide range of experimental conditions. This can be supported by the procedure to define the initial ranges and the improvement of performance. It is important to continue using this learning in different terpolymerization systems to define a generalized knowledge that describes innovative processes and CFs precursors that can be applied in traditional industrial processes, since the technology defined in this study is easy to be applied. Currently, several

TABLE 8: Terpolymerization conditions and characterization of TPRE.

Variable	Value	TPRE		
		$Conv$ (%)	\overline{Mv} (g/mol)	Es
A	60			
B	0.01			
C	3			
D	10%			
E	1%	33	95.81×10^4	3.1
F	MA			
G	IA			
H	1			
I	350			

Conversion rate ($Conv$); average viscosimetric molecular weight (\overline{Mv}); and extent of stabilization (Es) of TPRE developed by solution terpolymerization.

TABLE 9: Properties of developed precursor fibers.

FPAN	Linear density (dtex)	Elongation (%)	Tensile strength (cN/dtex)
FCOM	6.75	16.08	8.07
FPRE	4.00	12.11	16.87

studies are underway to analyze and compare quantitatively and qualitatively other comonomers and termonomers, other polymerization systems like suspension and modified spinning processes.

3.2. Physical-Mechanical Evaluation of Terpolymer and Resulting Precursor Fibers. Two terpolymers were used to develop FPAN. The first was based on AN-MA (PCOM) of commercial degree. The second precursor corresponding to the developed terpolymer was based on AN-MA-IA (TPRE). FPAN was obtained from PCOM (named FCOM), and FPRE was obtained from TPRE. The production of PCOM corresponded to a process of obtaining CFs precursors based on P[AN-MA]. Actually, PCOM is used in conventional carbon fiber applications. Therefore, PCOM was taken as a reference to compare FPRE because it is representative for common precursor fibers. The operation conditions in the wet spinning were the same for both FCOM and TPRE. Optical microscopy was used to observe the fiber morphology and physical-mechanical properties were determined. Table 9 and Figure 5 show the results of the characterization of FPRE and FCOM. Although both FPRE and FCOM were prepared under the same conditions, physical and mechanical differences were observed. Regarding the shape of the cross-section of the fibers, the shape of the FPRE was "circular", while that FCOM had a "bean" shape. These differences were obtained principally by the low coagulation velocity for the case of FPRE and the higher velocity of the FCOM where in the last case, the high coagulation velocity caused the fiber collapsing to obtain the "bean" shape, see Figures 5(a) and 5(b). In the coagulation process, the diffusion and counter diffusion rates of the solvent and nonsolvent define the morphology of the fibers. Diffusion processes can be controlled

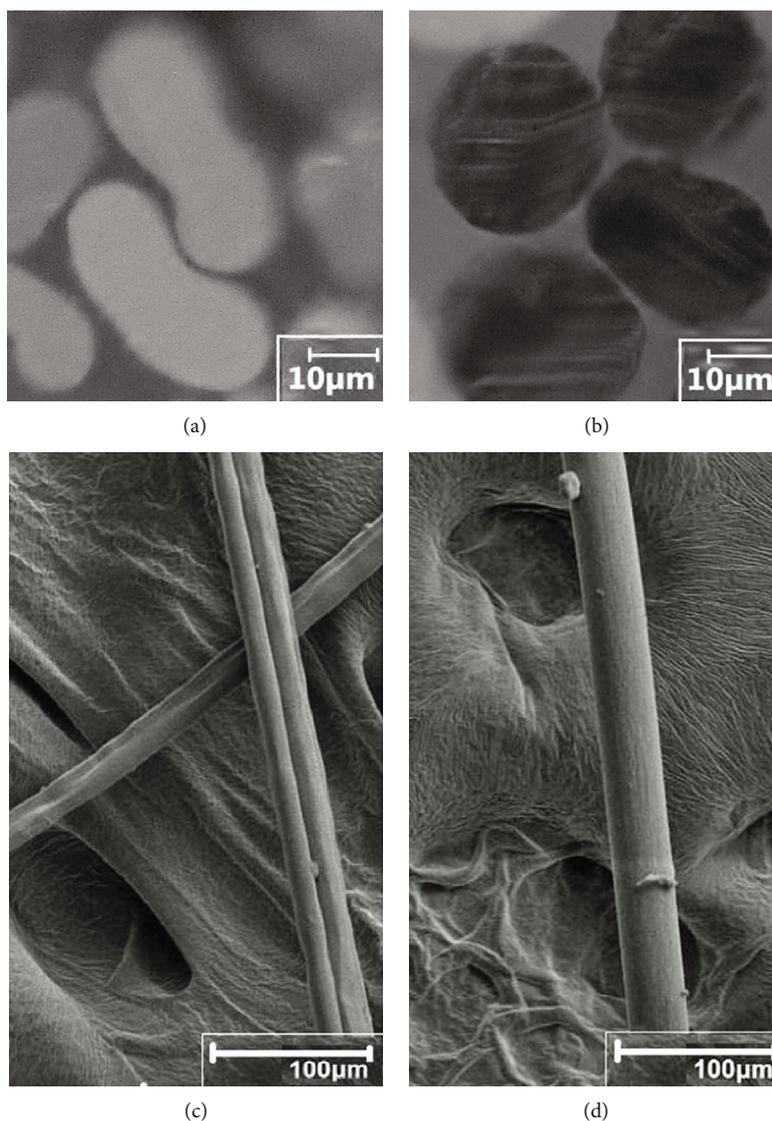


FIGURE 5: Longitudinal and cross-sectional morphologies of fibers. (a) and (c) for FCOM, (b) and (d) for FPPE. (a) and (b) obtained with optical microscopy, (c) and (d) obtained with SEM.

by diverse variables such as the solvent concentration in the coagulation bath, the coagulation temperature, the spinning solution concentration, the draw ratio, and the stereoregularity of the polymer [22, 50, 51]. The high concentration of solvent in the coagulation bath decreases the coagulation rate, resulting in more regular transverse shapes, that is, circular shapes [22, 52, 53]. The higher coagulation temperature accelerates the coagulation process, and the diffusion is deeper, allowing the fibers to take circular cross-section shapes due to the elimination of molecular stresses that cause the fiber deformation [52, 54, 55]. However, it was found that with coagulation temperatures above 60°C, the coagulation rate was so high causing the fiber cross-section becomes irregular [54]. FPPE showed a more uniform structure along the fiber axis, while the FCOM structure was less uniform, see Figures 5(c) and 5(d). On the other hand, the influence of the linear density (dtex) of the fibers on the mechanical properties was observed. The value of denier was related to

the fiber mechanical properties, and smaller diameter filaments had higher tensile properties [7]. Thus, the tensile strength of FPPE (16.87 cN/dtex) was greater than that of FCOM (8.07 cN/dtex) since the denier value of FCOM was twice than FPPE, see Table 9. This result indicates that fiber with greater molecular orientation can be obtained with TPPE compared to PCOM. The chemical composition of the precursor polymers plays an important role in the molecular structure of the fibers formed. The composition of the coagulation bath on the mechanical properties of precursor fibers based on P[AN-IA] was investigated, and it was found a maximum tenacity value of 8.2 cN/dtex and an elongation of 10.3% [56]. Other researchers have evaluated the precursor fibers based on P[AN-MA] with high molecular weight (>1,000,000 g/mol) and obtained fibers with high tensile modulus, but with high stabilization temperatures and low spinnability [5, 7]. The interactions between the chemical composition of the precursor and the coagulation

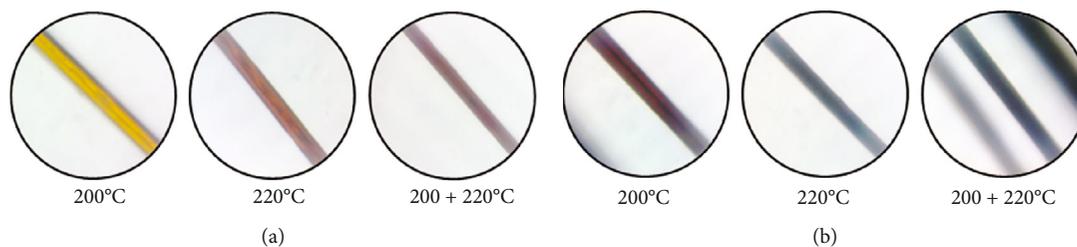


FIGURE 6: Optical microscopy, longitudinal section of fibers treated thermally at different temperatures and times. (a) for FCOM and (b) for FPPE.

medium have interactions that define the morphology of the fibers [1, 9, 25].

3.3. Effect of Thermal Treatment in Precursor Fibers. Optical microscopy of FPPE and FCOM thermally treated at different temperatures and times is shown in Figure 6. The change in coloration was more significant in FPPE than in FCOM in all cases. A darker coloration suggested a more complete stabilization by the chemical composition of the fibers. Conjugated structures and aromatic rings in the intermediate structure of the stabilized fibers were responsible for the color change and acted as a color agent [10, 57]. Although, it is believed that the dark coloration of fiber was due to the formation of a ladder structure, the study of the stabilization of FPAN through the change of coloration was not completely clear yet. As mentioned above, the use of an acidic termonomer, specifically IA, favored the cyclization reaction of the nitrile groups. The IA disrupts the nitrile-nitrile interactions allowing better alignment of the chains and acting as an initiator of the polymer formation in ladder structures, compared to FCOM that does not contain a termonomer. The variation in the stabilization results can be attributed to the different reaction mechanisms during the heat treatment influenced by the comonomers and termonomers and their distribution and arrangement of the polymer chains [6, 9]. In the first instance, this confirms that the chemical composition of FPPE induces a more efficient stabilization of the fibers.

FTIR spectroscopy was used to analyze structural changes of FPPE and FCOM with the thermal treatment. Figure 7 shows the FTIR spectra of FPPE and FCOM thermally treated. It was observed that the band of the $C\equiv N$ groups at 2243 cm^{-1} decreased its intensity with increasing temperature suggesting the advance of the thermal stabilization, while the band of the $C=C$ groups at 1595 cm^{-1} increased with temperature. FCOM showed a small extension of the stabilization reactions, since the peak intensity at 2243 cm^{-1} decreased slightly with the increase of the temperature. The changes of the FTIR spectra of FPPE show that the intensity in the band of the nitrile groups at 2243 cm^{-1} decreased significantly with the temperature. The increase in the intensity of the band at 1595 cm^{-1} indicated the formation of a greater number of $C=C$ and $C=N$ bonds. This extension of cyclization and dehydrogenation was promoted by the composition of PPPE and, specifically, by the termonomer IA [7, 8, 25].

The extension of the stabilization was determined using FTIR of FPPE and FCOM via the parameter E_s , where the graph of E_s versus temperature is shown in Figure 8. It was observed that FPPE showed higher E_s values than FCOM. This implies that FCOM needs a higher temperature to induce stabilization reactions: cyclization and dehydrogenation. FPPE favor the cyclization and dehydrogenation at a shorter time or a lower temperature. This confirms that the termonomer IA can significantly promote the stabilization of the precursor fiber. Figure 9 shows the DSC of both FPAN. It can be seen exothermic processes related to the cyclization reaction. The evolution of a large amount of heat has been attributed to the cyclization of nitrile groups and depends on the nature of the polymer and the experimental conditions. Cyclization is a highly exothermic process and, for homopolymers of PAN, it occurs at high temperatures ($\sim 307^\circ\text{C}$) [3, 8, 25]. Commercial precursor fibers based on P[AN-IA-MA] (from Courtaulds Ltd.) have been the basis for the study of thermal stabilization reactions, and some researchers found that the cyclization temperature was 220°C [1, 9]. The presence of comonomers facilitated the stabilization process since they acted as initiators of the cyclization reaction allowing the reaction to occur at a lower temperature. It can be seen that the start temperature of the FCOM reaction is 226°C , while it is 185°C for FPPE. The temperature of the peak maximum is 291 and 283°C for FCOM and FPPE, respectively. The final temperature is 322 and 324°C for FCOM and FPPE, respectively. The previous temperatures are lower than those of the homo-PAN. This confirms the results obtained with the FTIR analysis, where it has been observed that the decrease in peak intensity of the nitrile groups is more significant in FPPE than in FCOM.

4. Conclusions

Solution polymerization systems were analyzed and improved via experimental designs. Results indicated that it was possible to obtain remarkably attractive precursors from other systems for the low residence time reaction [2, 13, 17, 18, 29], good values of conversion reaction [29], and high thermal reactivity [8, 11, 13]. The use of the air atmosphere in the polymerization system was more robust, which is a new contribution in the design of carbon fiber precursors. These results showed that the extrusion system with new drying and collapsing zones allowed to improve the mechanical properties of the fibers and the texture of the filaments

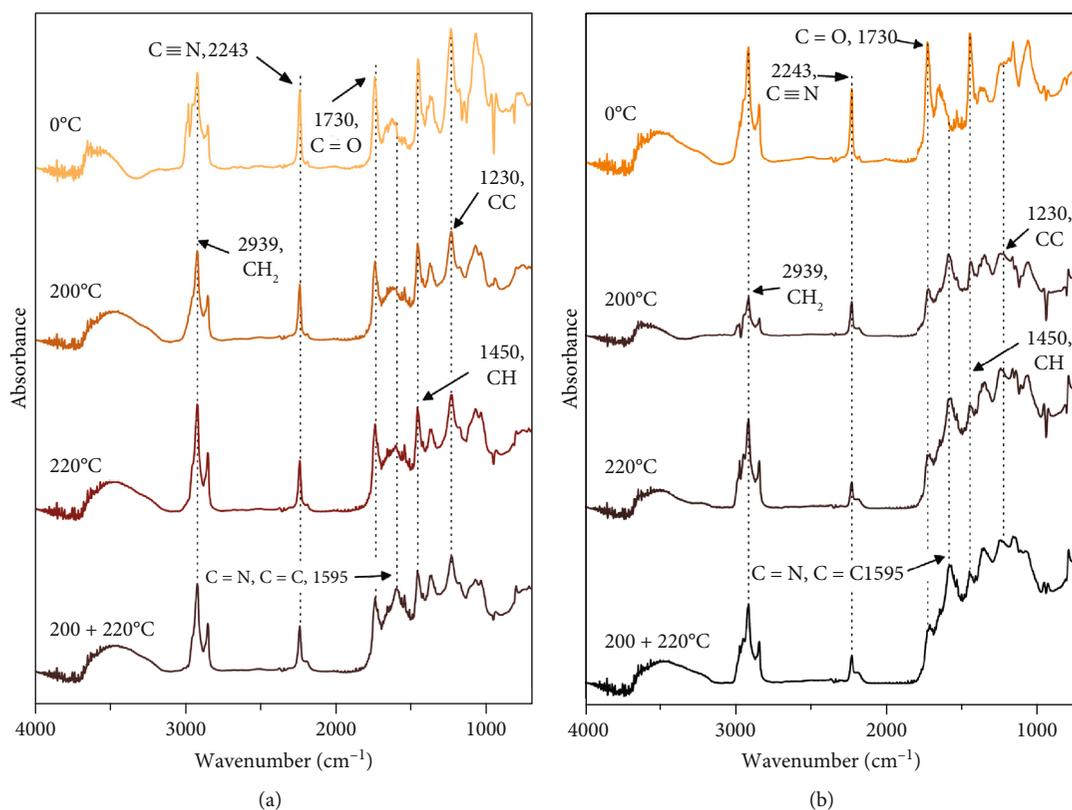


FIGURE 7: FTIR spectra of precursor fiber heated at different temperatures: (a) FCOM, and (b) FPRE.

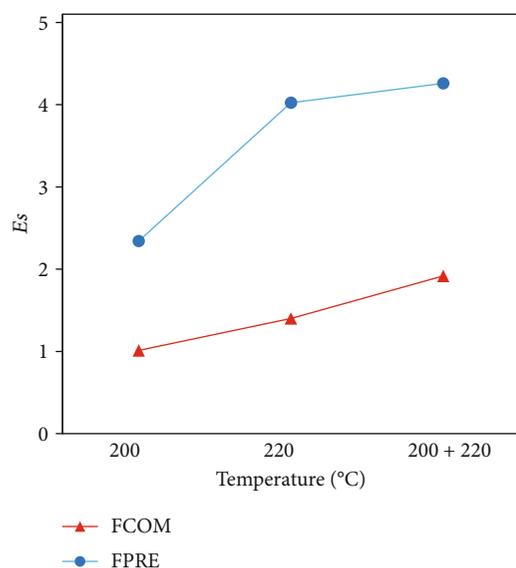


FIGURE 8: Extent of stabilization (E_s) of FPRE and FCOM heated at different temperatures.

surface. Two precursor polymers were developed and compared as CFs precursors in terms of their mechanical properties and structural changes in the stabilization stage. The chemical composition of FPAN is one of the critical characteristics that can alter the sequence and temperature range of stabilization reactions. The chemical composition of FPRE shows that the cyclization of nitrile groups is initiated at a

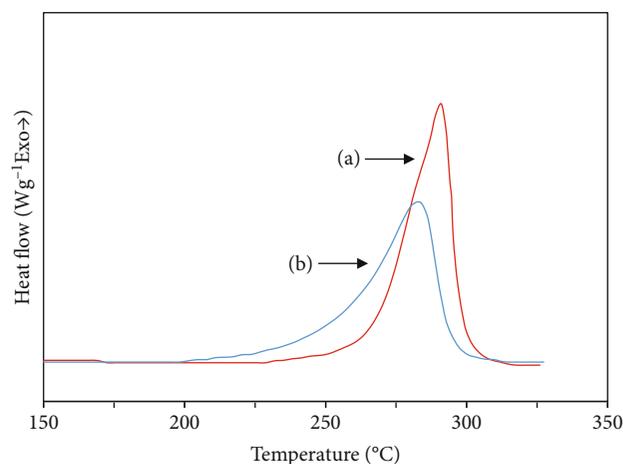


FIGURE 9: DSC of FPAN in air. (a) FCOM and (b) FPRE.

lower temperature than FCOM. The use of IA as termonomer favors fiber stabilization reactions, which could bring a positive impact on the economy of a global carbon fiber production process since it can reduce time and energy consumption to obtain a specific structural change of the precursor fibers. Studies on the mechanical properties of stabilized fibers are necessary to obtain an accurate comparison.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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