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Research Letter

Electrospinning of PAN/lignin blends aiming the production of carbon nanofibers

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Abstract

PAN electrospinning blends with different Kraft lignin (KLp) contents (10–50% by weight) were characterized via FT-IR, TGA and DSC and SEM. FT-IR analyzes identified typical functional groups of PAN and KLp in electrospinning mixtures. DSC and TGA data showed good thermal stability of the mixtures, which supports the subsequent fiber stabilization step. SEM images showed the mixture to be 50% by weight. of lignin, electrospun with a voltage of 18 kV, resulted in fibers with smaller diameters and fewer defects. Carbon blanket from the mixture with 10% by weight of LKp was successfully obtained.

Introduction

Carbon materials such as carbon microfibers and carbon nanofibers can be obtained from different precursors, especially pitch (mesophasic and isotropic) and natural or synthetic polymers, such as Rayon® and polyacrylonitrile (PAN), through the use of various techniques.[1–4] These materials, specifically these fibers, are very attractive for use in several advanced applications in industrial fields, such as aerospace and automotive, due to several properties related to high rigidity, good mechanical strength, low specific mass, and an appropriate aspect ratio (ratio of length to diameter).

Electrospinning is one of the main techniques with good productivity in obtaining fibers at micro and nanometer scales.[5] This process also has advantages for obtaining materials with a high surface area/volume ratio, high porosity, fibers with controlled diameter, composition, and specific morphologies.[6] This technique occurs through the application of an electric field, using a polymeric solution that results in mats with interconnected fibers. Considering this technique, mats based on PAN, lignin, and other polymeric solutions have been obtained, aiming at various applications, for example, in the production of carbon nanofibers.

The literature also shows interesting results involving the electrospinning of conductive solutions, for example, by incorporating conductive nanoparticles, and melted samples, aiming to obtain conductive nanofibers. However, these studies may present the formation of unwanted connections between the high voltage electrodes, favored by the electric field generated in the process, which result in electrical discharges. In this situation there is a major challenge to be resolved.[7] Li et al.[8]

obtained conductive electrospun mats by co-electrospinning trimethylethoxysilane (MTES) and a conductive polyvinylpyrrolidone (PVP)/graphene solution, subsequently removing the PVP by heat treatment at 500°C. The mats obtained showed electrical conductivity of up to almost 2000 S/m. Wang, Naguib, and Bazylak[9] electrospun conductive fibers via two different routes. Firstly, polystyrene (PS) mats were obtained with the addition of multi-walled carbon nanotubes (MWCNT) (from 1 to 10% wt). In a second route, $FeCl_3$/PS oxidizing fibers were electrospun and then exposed to pyrrole monomer (Py) in a vacuum chamber. The authors observed that mats with the conductive polymer coating showed much higher electrical conductivity than those with CNT filler.

PAN is derived from petroleum, and it is the most used raw material to obtain carbon fibers due to its high content of fixed carbon (45–55% wt). This polymer is characterized by not being fusible when subjected to proper heat treatment and when it is heating above 180ºC, the cyclization of nitrile groups occurs with the release of energy and gases. For the production of carbon fibers, as a first step, PAN is slowly heated under tension, to increase its glass transition temperature (Tg) and to become stable for the next step, the carbonization process. This stabilization process is very important to obtain carbon fibers with adequate properties. However, as consequence, increases the time process and the production costs.[10,11]

Lignin is a promising precursor of low-cost carbon materials from renewable origin, being a macromolecule of great abundance and with a phenolic chemical structure rich in carbon atoms.[12,13] Around 50 million ton of Kraft lignin (KL) are produced each year as a by-product of the pulp and paper industry,

while only 2% is used for medium and low-cost applications. Currently, most of lignin is burned for energy generation.[14] The high abundance and aromatic character of this material are of great importance for further economic use in high value-added products, such as carbon fiber precursors, for instance.[15]

However, despite the visible advantages of using lignin, the fibers produced from this precursor usually have inferior mechanical properties when compared to those obtained with other carbon fiber precursors. Furthermore, to use lignin as a precursor, it has to be processed by spinning or by another process technique, such as electrospinning. Meanwhile, the electrospinning of Kraft lignin is a major challenge, due to its low molecular weight and low solution viscosity, which results in non-uniform fiber formation and, in many cases, no fiber formation.[16]

The lignin solution, when electrospun alone, results in an electrospray of particles due to the lignin not creating sufficient chain entanglements among the molecules and within the solution. In the literature, approaches for electrospinning lignin are found, such as mixing it with a second polymer (binder polymer), co-electrospinning, and solvent fractionation to remove low molecular weight fractions.[16]

Many studies use PAN/lignin blends to obtain defect-free and homogeneous fibers. Mustafov et al.[12] prepared PAN/KL blends with up to 85% lignin in the blend and observed that increasing the lignin content results in a decrease in solution viscosity, consequently decreasing the diameter of the fibers produced.[12] Camargo (2019) prepared PAN/KL blends in the ratios of 50:50, 40:60, 30:70, 20:80, and 10:90 and showed that with the increase in the amount of lignin in the blend, there was a decrease in viscosity of the solution and a decrease in fiber diameter.[2]

Thus, the purpose of this work was to carry out a study involving the electrospinning of blends of PAN and Kraft Lignin, with different lignin ratios (10–50 wt %) to obtain polymeric fibers mats and to establish a preliminary study of them to become suitable for the production of carbon nanofibers.

Materials and methods
Materials
Polyacrylonitrile (PAN), $\overline{M_n} = 267,000$ g/mol, was supplied in powder form by Racidi Fibras Company (Brazil). Kraft lignin was provided by Suzano Papel and Celulose SA. (Brazil). The solvent used for the processing of the mats was N,N-dimethylformamide (DMF) (PA 99%) from the company Neon Comercial Reagentes Analíticos Ltda (Brazil).

Lignin purification
The KL purification was conducted in accordance with the literature.[17] Around 100 g of KL were dissolved in 400 g of the DMF solvent under magnetic stirring for 4 h. Afterwards, the solution was filtered using a stainless-steel mesh of 75 μm and the soluble fraction was added in a deionized water acidified (pH 2.0) for the precipitation of lignin. The

precipitated lignin was filtered under vacuum, washed with acidified deionized water, and dried. After completing the purification process, the lignin was dried in a vacuum oven (Vacucell) at 45°C for 42 h. In this work, the purified Kraft lignin was named as LKp.

Preparation of the polymer solution
PAN/LKp solutions were prepared in the proportions of 90/10, 80/20, 70/30, 60/40, and 50/50 wt %, keeping the solution concentration in 15% wt Firstly, PAN was solubilized in DMF at 45°C in a bottom neck glass flask under magnetic stirring for 1 h. Afterwards, the LKp was added to this solution, remaining under magnetic stirring for 2 h at (25 ± 2)°C.

Viscosity analysis
Before the electrospinning process, viscosity values were obtained for each solution, to identify the influence of different lignin contents on the viscosity of the polymeric solution. For this, a Brookfield DV-II T viscometer (model SC4-27), adapted with a stem number 29, was used. The analyses were carried out at room temperature $(25 \pm 2°C)$ using 7.1 mL of sample.

Electrospinning process
The apparatus used in the electrospinning process in this work has a high voltage supply (Faísca), a grounded collector rotating cylinder, a syringe pump (Legato 220, KDS Scientific), and a 20 mL glass syringe with a stainless steel with diameter of 1.0 mm and length of 25 mm.

The voltage parameters used for electrospinning the blankets were 15 kV (sample 90 /10% wt); 17 kV (sample 80/20% wt); 18 kV (70/30% wt sample); 19 kV (60/40% wt sample) and 19 kV (50/50% wt sample). The fixed process parameters of the electrospinning were: solution flow rate of 0.05 mL/min, working distance of 10 cm, and a cylinder rotation of (36 ± 1) rpm. The voltages (V) used to produce the fibers

Table I. Glass transition temperature (T_g) of PAN/KLp electrospun mats, exothermic peak enthalpy (ΔH) and cyclization temperature (T_2).

Sample	T_g [ºC]	*T_2 [ºC]	ΔH [J/g]
PAN	87	313	508.0
90/10	108	315	494.7
80/20	114	316	667.1
70/30	116	315	273.2
60/40	113	317	544.4
50/50	117	319	339.6
KL	119	–	–
KLp	127	–	–

*T_2—Cyclization/oxidation temperature.

varied from 15 to 19 kV. Table I shows the parameters used for the electrospinning of PAN/KLp mats.

Characterization of electrospun blends
Fourier transform infrared spectroscopy (FT-IR)

PAN, KLp, and PAN/KLp mats in the proportions of 90/10, 80/20, 70/30, 60/40, and 50/50% wt were analyzed by FT-IR spectrometry (PerkinElmer Spectrum 100 FTIR) with attenuated total reflectance (ATR) accessory system. The spectrum was obtained from 4000 to 400 cm^{-1} with 32 scans and resolution of 4 cm^{-1}.

Scanning electron microscopy (SEM)
The morphology of the mats was analyzed by SEM (FEI INSPECT S50). Before analysis, the samples were glued to the holder and were coated by a thin layer of gold. The average diameter of the fibers and their diameter distribution were determined by measuring 100 fibers for each sample using image analysis software (Image J®).

Thermal analyses
Thermogravimetric analyses (TGA) of PAN, KLp, and PAN/KLp mats were investigated using TGA equipment (SII Nanotechnology TG/DTA 6200). Around 3 mg of each sample were heated from 60 to 1000°C, under nitrogen atmosphere and flow rate of 20°C/min^{-1}.

The thermal transitions of the electrospun mats were conducted by differential scanning calorimetry (DSC) (TA Instruments, series Q20). The analyses were carried out in nitrogen atmosphere, using approximately 1 mg of sample. Two thermal cycles were performed. The first cycle was carried out in a temperature range of 25 to 300°C, under a heating rate of 30°C/min, to obtain the enthalpy values of the exothermic peak. The second cycle was carried out from 25 to 220°C, under a heating rate of 30°C/min to determine the T_g of the electrospun mats.

Preliminary study aiming the production of carbon nanofibers
The thermal stabilization and carbonization were performed in an electrical oven with cylindrical camera of quartz.

The stabilization of the mats was started by heating the sample under air atmosphere from 25 to 300°C under a heating rate of 2°C/min and holding at 300°C for 2 h.

The carbonization process was conducted in two steps. Firstly, the sample was heat from 25°C until 500°C at 3°C/min due to the significant weight loss of volatiles after stabilization process occurs in this temperature range. After, the sample was heated from 500°C to 1000°C at 10°C/min and it was kept in this temperature by 1 h.

Results and discussions
Viscosity of solutions
The change in the viscosity of the solution was verified, according to the lignin content in the blend. For samples with 10% wt, 20% wt, 30% wt, 40% wt and 50% wt, values of 1230 mPa.s, 830.8 mPa.s, 143.8 mPa.s, 167.3 mPa.s, 56 0.44 mPa.s. were obtained. As the lignin content in the solutions increases (from 10 to 50% wt), the viscosity of the samples decreases continuously. Similar behavior is reported in the literature and is attributed to the low intrinsic viscosity that lignin imparts to solutions.[18] Schreiber and collaborators[19] observed the same behavior when analyzing the effects of lignin content on the viscosities of poly(ethylene oxide) (PEO)/lignin solutions, reporting that increasing the lignin content by up to 40% resulted in a decrease in the viscosity of solutions.
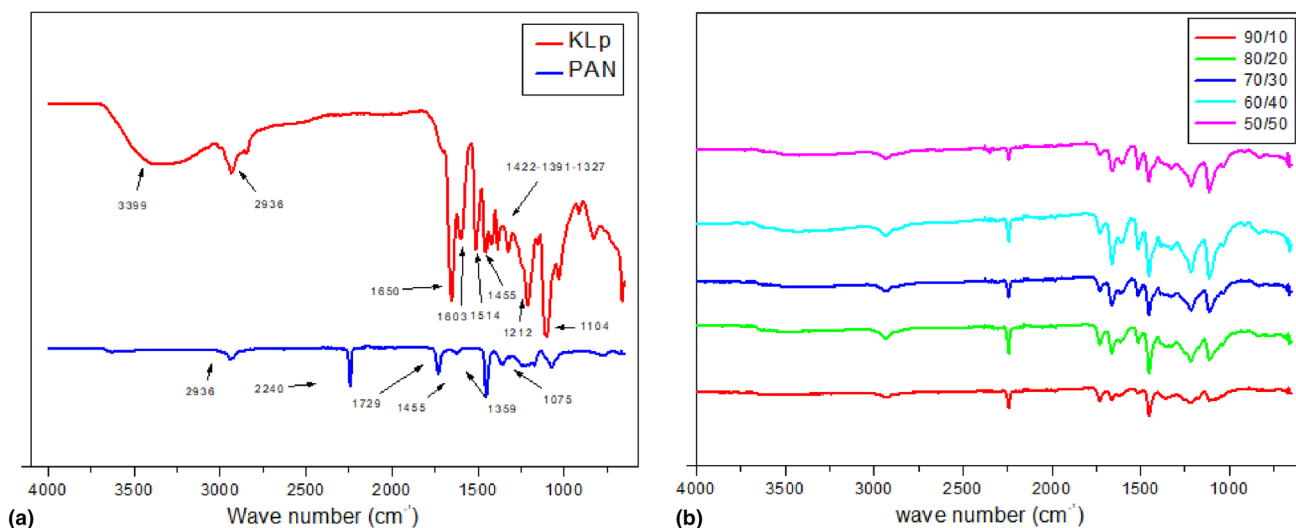

Figure 1. FT-IR spectra of the samples: (a) neat PAN and LKp and (b) PAN/KLp mats.

Fourier transform infrared spectroscopy

FT-IR spectroscopy was used to identify the functional groups and chemical bonds present in the PAN/KLp mats obtained by electrospinning. Figure 1 presents the spectra obtained for neat KLp and neat PAN [Fig. 1(a)] and for the PAN/LKp blends-based mats with concentrations varying from 10 to 50% wt of lignin [Fig. 1(b)].

Figure 1(a) shows in the spectrum of the purified lignin the presence of following bands: at 3399 cm^{-1} attributed to the OH stretching of aliphatic hydroxyl groups,[20,23] at 1422 cm^{-1} assigned to aromatic ring vibration combined with in-plane C-H deformation,[22,23] at 1604 cm^{-1}, characteristic of C=O stretching in aryl ketone aromatic ring vibrations, which indicates a greater amount of syringyl (S) units than guaiacyl group (G), and at 1327 cm^{-1} referring to the condensed S-ring.[22] In the PAN spectrum, bands at 1359 cm^{-1} and 1075 cm^{-1} are visible, related to the polar-polar interaction between the S=O and C≡N groups.[24] These bands are typical of PAN and are not observed in the blends, as shown in [Fig. 1(b)]. It also can be found a band at 2936 cm^{-1}, which corresponds to the CH stretching of aromatic methoxyl groups and methyl and methylene groups of side chains. However, in the mats, this band becomes smaller, with the increase of the lignin content, almost disappearing in the blend with 50 wt%. of lignin which is in agreement with the literature.[4,24–26]

At 2240 cm^{-1}, 1729 cm^{-1}, and 1455 cm^{-1} characteristic PAN bands are present in both polymer and blends. The band at 2240 cm^{-1} can be attributed to the stretching of C≡N bonds[4,26,27] or residual solvent (DMF)[27,28] and the band at 1455 cm^{-1} refers to the vibration of aliphatic CH groups (CH, CH$_2$, and CH$_3$).[4,26]

Related to KLp, it can be found in polymer blends a band at 1604 cm^{-1}, attributed to C=O stretching. As the content of KLp increases the intensity of this band.[22,23,25] This same behavior occurs with the bands at 1514 cm^{-1} and 1455 cm^{-1}, corresponding to aromatic structural vibrations (G>S)[21,22] and the deformation of the O–CH$_3$ bond (CH asymmetric deformations in C–H$_3$ and C–H$_2$),[21] respectively.

The band located at 1212 cm^{-1} is attributed to the stretching of carbon–carbon and carbon–oxygen bonds, with single and double bonds (C–O and C=O), while the band 1114 cm^{-1} indicates the stretching of C–C, C–O, and C=O. Both are characteristics of lignin, and they remain visible in the blends at a lower intensity.[21,29]

Scanning electron microscopy of the electrospun blends

The influence of the concentration of the KLp concentration in the electrospun PAN/KLp blends on morphology of the mats was evaluated, as shown in Fig. 2.

The electrospinning of the mats with 10% wt of lignin, as shown in [Fig. 2(a)] was possible to obtain mats with fibers
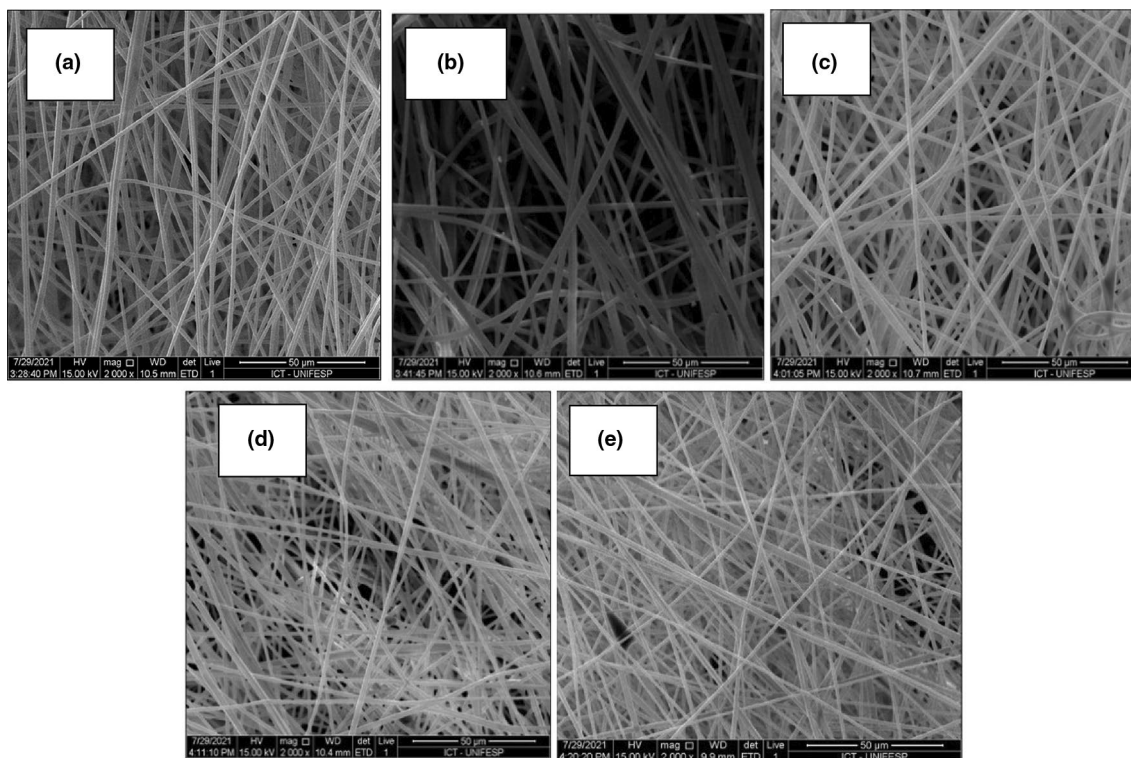

Figure 2. SEM of samples (a) 90/10–15 kV, (b) 80/20–17 kV, (c) 70/30–18 kV; (d) 60/40–19 kV; (e) 50/50–19 kV.

without defects, uniform and with high number of fibers in the blend with 10% wt of KLp, at 15 kV.

However, increasing the concentration of KLp, higher voltages were used to obtain fibers without defects. Defect-free and uniform fibers were obtained in the blend with 20% of lignin when electrospun at 17.2 kV, as shown in [Fig. 2(b)]. Higher voltage, 18 kV also was used for obtain fibers in the blends with 30% wt lignin [Fig. 2(c)] favored the formation of fibers, with a high amount fibers deposited on the collector, and with few defects.

It was possible to electrospun PAN/LKp with 40% wt of lignin at 19.5 kV [Fig. 2(d)]. In the mats with 50% wt of lignin, no significant presence of defects in fibers was observed, using voltage of 19 kV to process them, as shown in [Fig. 2(e)]. Above 19 kV only a few amount of fibers were formed due to destabilization of the jet, preventing the fibers from reaching the collector.

As a general behavior, as the amount of KLp increases in the blends, higher voltages are used to obtain fibers without defects.

The average diameter (AD) obtained from 100 fiber measurements for each sample was measured. The fibers of the blankets with 10% wt, 20% wt, 30% wt, 40% wt and 50% wt, had an average diameter of 1.52 μm, 1.98 μm, 1.66 μm, 1.37 μm and 1.20 μm, respectively.

The addition of lignin is inversely proportional to the diameter of fibers, that is, the higher the percentage of lignin in the blend, the smaller the average diameter of the fibers. In the mats with 50% wt of KLp, there was a decrease of about 39% in the diameter of the fibers, when compared with the samples with 10 and 20% wt of KLp, which have fibers with diameters of 1.52 and 1.98 μm, respectively. These results are associated with the behavior observed in the viscosity measurements (Fig. 2), where the increase of lignin in the solutions decreased the viscosity of samples. Based on the literature statements, this behavior can be explained by the lower molecular entanglement of the PAN polymer chains, with the increase of lignin concentration in the solutions, which contributes to a decrease in the viscosity of solutions and provided smaller diameters of fibers.[2] This effect was also observed by Jiang et al.,[11] who attributed it to the decrease in the viscosity of the spinning solution caused by lignin, and by Li et al.,[30] who associated the decrease in average fiber diameters to the combination of increasingly lower viscosities and the increase in electrical conductivity in the solutions provided by lignin. According to Li et al.,[30] when the viscosity of a solution is low, the entanglement among the polymer chains is lower, thus decreasing the jet resistance, causing the charged droplets to break into tiny particles.

Thermal properties

Table I presents the thermal transitions of these samples.

The PAN polymer has an exothermic peak at 313°C, attributed to the oxidation and cyclization processes of the structure.

This event refers to the exothermic reaction involving the nitrile group with adjacent groups.[8]

The glass transition temperature (T_g) of polymers was recorded at the midpoint of the heat capacity transition temperature of the second heating run, as described by Gorgobyl et al.[1] However, this transition is difficult to determine for lignin due to the interactions between the hydrogen bonds that can be formed during heating which can change the original T_g of lignin sample and also due to possible degradation of the amorphous structure of Kraft lignin.[32,33]

It can be seen higher value of T_g for the KLp when compared to the unpurified sample. According to Sameni et al.,[31] this alteration in the T_g occurs due to the removal of impurities present in lignin. The purified Kraft lignin has a melting temperature (T_m) at 208°C and a sharp endothermic peak referring to the initial degradation temperature at 255°C. In the electrospun blends, nearly values of T_g (113–117ºC) can be found, except for the blend with 10% wt of KLp, which presents a slightly lower value (108ºC), when compared to the other blends. This value is attributed to the higher amount of PAN in this blend. The blends also present exothermic peaks referring to the cyclization and oxidation of the structure. The increasing cyclization temperature, from 313 to 319°C, occurs with the increasing lignin content in the blend. Opposite results were reported by Jiang et al..[11] They found that the increase in lignin content in the blend results in a decrease in the cyclization temperature of the polymeric mats and increases the exothermic enthalpy. This behavior was attributed to the carbonyl/carboxyl groups of lignin being able to initiate the cyclization reaction. In this case, it is worth noting that lignin composition can vary greatly from batch to batch and different regions.[11]

Thermogravimetric analysis was carried out to evaluate the thermal degradation behavior of the electrospun mats and, also, their conversion into carbon.

The PAN has at least two degradation stages: at 243°C and 457°C, which can be attributed to C-N bonds and ends with C–C breakage of the PAN, followed by the volatilization of gases present in the sample at approximately 500°C, such as H_2O, CO_2, CO, CH_4, NH_3, and HCN.[2] According to Sameni et al.,[31] PAN begins to decompose at temperatures close to 300°C, with the occurrence of pyrolytic reactions, cyclization, and oligomerization of the nitrile groups of PAN, forming rings.

The thermal degradation of the lignin shows three steps. Initially, in the range of 40 and 104°C (steps 1 and 2), a small weight loss which probably can be due to the evaporation of moisture. The third stage occurs at 261°C, which can be attributed to the thermal degradation of the macromolecule. Gordobil et al.[1] found similar result in the thermal decomposition of softwood Kraft lignin, where they identified degradation steps at 55, 262, and 390°C, with a residue of 38%. According to Camargo,[2] the thermal decomposition of lignin gives rise to volatile products with low molar masses, due to its heterogeneous chemical structure. Water, formaldehyde, methane, and methanol are the main products released in the thermal
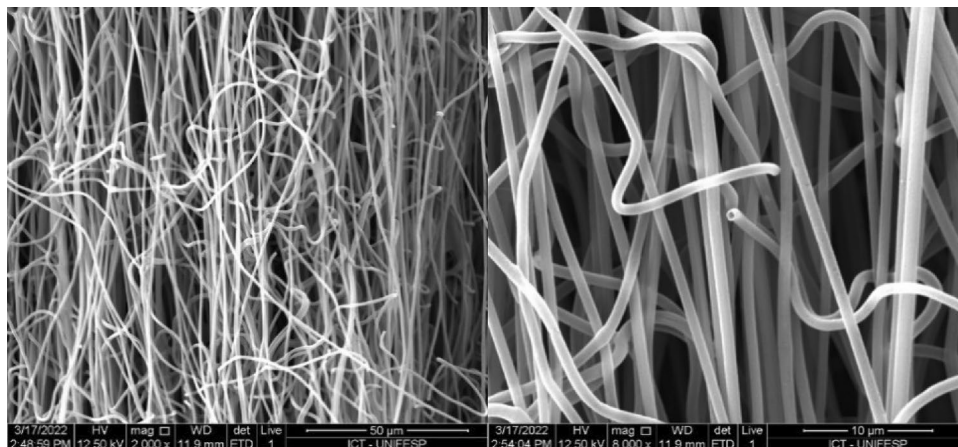
Figure 3. SEM of the carbonized PAN/KLp mat in the proportion 90/10 (%wt).

decomposition of lignin.[2] Lignin has a higher amount of solid residue (coal) (36,6%), when compared to PAN (27,8%),due to its greater aromaticity and the presence of inorganic components in its composition.

The electrospun PAN/KLp mats were also characterized via thermogravimetry.

All mats present a wide decomposition event, starting at approximately 150°C, attributed to the aromatic groups present in lignin.[12] Initially, a weight loss is observed in the TGA curve at 90°C, possibly due to the presence of moisture or low molecular weight fractions in the mats. Subsequently, a second weight loss is observed between 150 and 230°C, probably due to the presence of dimethylformamide since its boiling temperature is 153°C.[2] The main weight loss of the mats occurs between 200 and 500°C, indicative of the decomposition of lignin. According to,[28] small amounts of aromatic volatiles are released in this temperature range. The first weight loss of the blends can be attributed to the thermal degradation of lignin which occurs between 240 and 255°C, with values between 9 and 15%. The second stage of degradation takes place between 320 and 500°C, being attributed to the which can be attributed to C–N bonds and ends with C–C breakage of the PAN and also breaking of C–C bond[32] with the rearrangement of the phenolic structure of the lignin.[28] However, it is observed that, as the lignin content in the blend increases the Td_2 decreases from 457 to 329°C, decreasing its thermal stability. It is still possible to observe a small weight loss between 60 and 117°C, which can be attributed to the release of structural water, as well as the evaporation of the solvent used (DMF).[20,27] However, despite the lower thermal stability, as the amount of lignin in the blend increases, there is a higher amount of solid residue related to the content of carbon yield at the end of process. Similar behavior was verified by Nahra.[17]

The final carbon yield is a very important result in the production of carbon fibers, as higher weight losses during processing or low carbon yields result in higher processing costs. Thus, the carbon yield is directly related to the cost of the product.[28]

Scanning electron microscopy of the carbonized samples

Figure 3 shows the morphology of the PAN/KLp 10% wt of lignin mat after the carbonization process.

The carbonized mat present well-defined fibers with homogeneous diameters (0.40 ± 0.05 µm). It is also seen the occurrence of the rupture of some surface fibers significant decrease in the weight loss around 80%, and in the average diameter of the fibers with value around 70%.

Jayawickramage, Balkus, and Ferraris[34] studied the production of carbon fibers from PAN/lignin blends. After carbonization, the author obtained fibers with diameters of smaller than 100 nm and verified that the fibers maintain their morphology even after carbonization at 1000°C, forming independent and flexible mats.

Conclusions

In this work it was possible to produce electrospun blends of PAN/KLp until 50% wt of KLp. However, as the concentration of KLp increases, the voltage to produce the mats without defects need to be increased and the fiber diameters decrease. The blend with 50% wt of lignin in its composition, electrospun at 18 kV, presented the smallest fiber diameter values (1.20 µm) and the lowest number of defects. FT-IR analyses showed a decreasing in the band at 2936 cm^{-1}, which corresponds to the CH stretching of aromatic methoxyl groups and methyl and methylene groups of side chains of PAN with the increase of the lignin content, almost disappearing in the blend with 50% wt of lignin. DSC analyses showed no significant change in the T_g values for blends with KLp concentrations in the range of 20 to 50% wt of KLp. The addition of KLp shows a decrease in the exotherm peak and did not change the cyclization temperature. TGA showed that the increase in the lignin amount in the blend resulted in higher carbon yield at the end of the heat treatment, which makes them suitable for obtaining carbon fibers. The carbonization of the electrospun mat with 10% wt KLp, after oxidative thermal

stabilization, resulted in a homogeneous carbon mat, free of defects and with the average diameter of fibers around 70% smaller than those observed for the electrospun PAN/KLp mat.

This study proved that the electrospinning of PAN/lignin solutions is a promising process for the production of carbon mats, but other challenges in this matter exist and require further studies, such as the optimization of the electrospinning process and the carbonization process for the production carbon mats on a larger scale.

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Author contributions

ILRC: conceptualization, formal analysis, research, methodology, project administration, writing—preparation of original draft, writing—proofreading and editing. LSM: experimental support. LRN: experimental support. RRL: experimental support. LMG: conceptualization, formal analysis, research, methodology, supervision, writing—preparation of original draft. MCR: conceptualization, formal analysis, acquisition of funding, research, methodology, supervision, writing—preparation of original draft, writing—proofreading and editing. ECB: conceptualization, formal analysis, acquisition of funding, research, methodology, project administration, supervision, writing—preparation of original draft, writing—proofreading and editing.

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Data availability

The data generated in this studies are available in this article.

Declarations

Conflict of interest

The authors declare no conflicts of interest.

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