ANALYSIS OF POLYACRILONITRILE/LIGNIN BLENDS BY SEM AND FT-IR AS AN ALTERNATIVE PRECURSOR FOR CARBON MATERIALS

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https://doi.org/10.21452/bccm4.2018.14.05

Abstract

Lignin has been investigated as a promising feedstock for production of low-cost carbon materials. The kraft lignin was studied in this work since it is a waste from a production process at pulp and paper factory. Currently fibers from polyacrylonitrile (PAN) are precursors for obtaining carbon fiber, but at very high costs. In the first step of this work, blends with polyacrylonitrile and kraft lignin were investigated. The methodology employed was the extrusion process at temperature of 200ºC. Extrusion process is an economically viable and technologically robust process for the production of low-cost carbon materials from lignin precursors. The low cost and high availability of lignin have brought interest on its use as precursor of carbonaceous materials like activated carbons, carbon catalysts or composite materials. Copolymerization with conventional commodity plastics, particularly polyacrylonitrile (PAN), has gaining attention. This can be accomplished by an innovative technology for polyacrylonitrile-based precursors for carbon fibers, where lignin is mixing with the PAN in appropriate amounts to produce a polymer blend through a conventional extrusion process. The investigation revealed the production of good blends without disconnectedly phases inter polymers, based on the results of Scanning electron microscopy (SEM). FTIR analysis were also used to investigate the interaction inter polymer in the blend after the extrusion process.

1. INTRODUCTION

New carbon materials produced directly from biomass have gained a lot of interest on last years [1]. Biomass is an important feedstock for the renewable production of fuels, chemicals, and energy [2]. Recently, it has been shown that lignin is potentially a suitable precursor material for the production of carbon fiber and composites [3, 4]. Lignin is an aromatic heteropolymer that is mainly found in the secondary wall of wood cells and, after cellulose, it is the most abundant and important polymeric organic substance in the plant kingdom [5]. In Brazil there is large availability of many industrial wastes with high potential for lignin production. Industrial wastes deeply studied as raw material for carbon fiber precursors are the black liquor (from pulp and paper), sugarcane bagasse and Brazil nut shell waste. The production in 2012 of black liquor was 21,461 ton [6]. According to the MAPA [7] the industrial production of sugarcane bagasse during harvest from April 2015 to January 2016 was 186,214,322.08 t [7]. The production of Brazil nut is being increased every year and it is becoming a new line of research of great potential in the production of lignin in Brazil. Lignin-blends, like PAN-lignin (PAN = polyacrylonitrile), were a step ahead in this direction. In this work, new method to produce precursors to carbon materials containing lignin it was investigated. The methodology to obtain copolymer PAN-Lignin fibers evaluated herein is the extrusion process. It worth to mention that as a solvent free process it has great economic and ecological prospects. Lignin contains both hydrophilic and hydrophobic groups in its composition and PAN is the macromolecule with –CN dipole group to be preferably attracted by substances with hydrogen dipole interactions. The formation of cooperating bonds with neighbor carbons and formation of a copolymer PAN-lignin were tested. Glycerol, which is a by-product of biodiesel production and was used in the preparation of the blend samples, is a natural organic plasticizer to PAN-lignin blends. A key issue is the interaction of glycerol with PAN-lignin that exhibits high compatibility owed to chemical characteristics of interaction of the hydrogen dipole [9]. The objective of this study was to investigate a PAN-co-styrene (10%) / lignin blends as a possible precursor material suitable for production of carbon fiber, using an environmentally friendly process, since no organic toxic solvents are required.

2. EXPERIMENTAL PROCEDURE

2.1 Extrusion Process

The copolymer PAN-co-styrene (10%) / lignin blend was obtained by melt spinning process with glycerol as a plasticizer. The process was based in two stages: (1) formation of pellets of PAN-lignin plasticized with glycerol and additives through extrusion and, (2) PAN-lignin tapes production in extrusion equipment. The basic methodology was developed and the respective basic procedure will be following described. Proportions of 5%, 10%, 15% and 20% of lignin were used with PAN-co-styrene (10%) to manufacture the blends.

In stage 1: It was produced pellets of blend PAN-co-styrene (10%) / lignin plasticized with glycerol in the extruder. Various proportions PAN-co-styrene (10%) / lignin blends were tested to obtain formulations of the PAN-co-styrene (10%) / lignin blends. Figure 1 shows a schematic representation of the first extrusion step for copolymer precursors. The compound was prepared by mixing PAN-co-styrene (10%) and lignin powders, glycerol and other additives in appropriate amounts. The pre-extrusion compound was homogenized and fed in the extruder equipment to obtain polymer blend pellets. Afterwards, the polymer was thrown into feed hopper of the extruder equipment. The molten copolymer was compressed up a die with circular duct of diameter of 6 mm to conform in the shape of polymer blend tape. Then, the tape passed to a pelletizer that cut, through a rotary knife, the material that turned into pellets of plasticized PAN-co-styrene (10%)/lignin. These pellets were collected and stored.

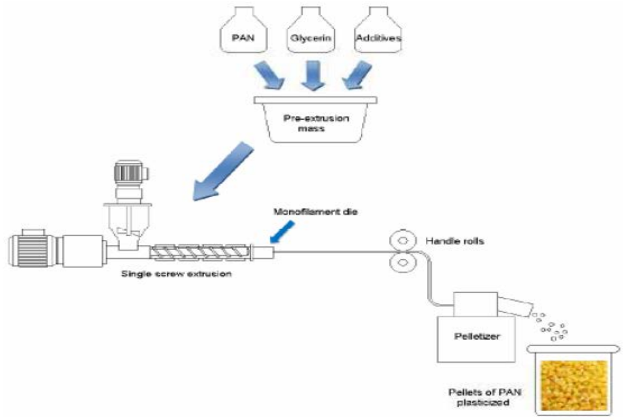


Fig.1. Stage 1: Illustrative scheme for obtaining the co-polymer PAN-lignin plasticized with glycerol in an extruder to produce pellets [4].

The next step was the production of PAN-co-styrene (10%) / lignin tapes by extrusion. It was comprised by a system that extends from the extrusion of pellets to the PAN-co-styrene (10%) / lignin blend winding tapes [9].

At the Stage 2: The pellets undergo melting and begin to flow at the screw extruder. Figure 2 shows scheme of the extrusion equipment to obtain the PAN-co-styrene (10%) / lignin tape. The dissipation of gases occurs during this event.

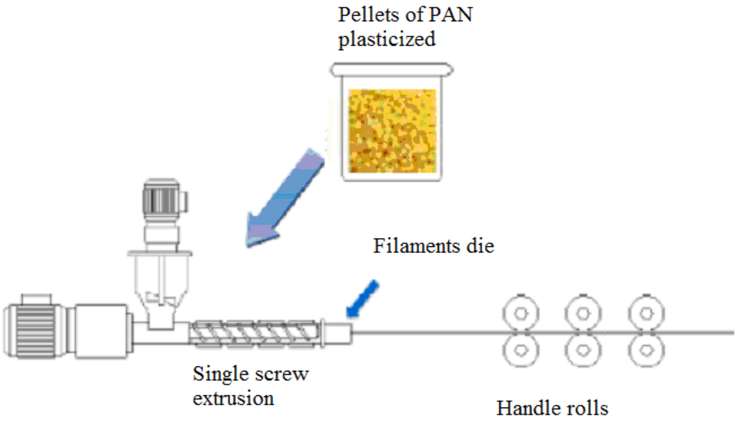


Fig.2. Stage 2: Illustrative scheme for obtaining PAN-co-styrene (10%) / lignin tapes in the extrusion equipment.

This work discusses the study that is undergoing using an environmentally friendly process. Since no organic toxic solvents were used, by using renewable and cheap sources of carbon (lignin). For the characterization of blends, instrumental methods were used, i.e., Fourier Transform Infrared (FTIR) and Scanning Electron Microscopy (SEM).

2.2 SEM micrographs

SEM micrograph analyses were done in room temperature after the gold sputter coating application on the surface of tape samples. The analyses parameters were: SEM High Voltage -

HV: 20kV, Wavelength Dispersive - WD: 9.85 mm, SEM Magnitude - MAG: 3.00 kx, and view filed on 69.2 um. This equipment is located in the Micrograph Laboratory at Dep. Mechanical Engineering, Instituto Tecnologico de Aeronautica - ITA.

2.3 FTIR

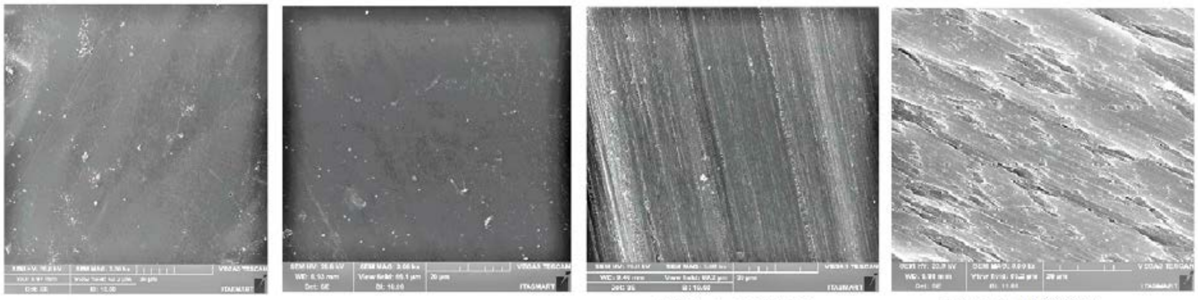
FTIR analyses were performed on Spectrum One - PerkinElmer, in the medium infrared (MIR) region by obtaining reflection spectra with universal attenuated total reflection accessory (UATR), 120N torque, 20 scans, in room temperature, without any previous preparation of the samples. This equipment is located at laboratory of Instrumental Analyses (LAAI), Division of Chemistry (AQI), Institute of Aeronautics and Space (IAE).

2.4 MATERIALS

Hardwood kraft lignin was provided by Fibria. Lignin was blended with PAN-co-styrene (10%) using the procedure described by Quimlab [Alves 2007; 2011]. PAN-co-styrene (10%) is named henceforth as PAN. Glycerol was used as plasticizing agent. The employed extrusion equipment was domestic homemade equipment developed by Quimlab.

3. RESULTS AND DISCUSSION

The SEM micrographs blends manufactured by extrusion process are shown in Fig. 3. The mixing ratios used were 5% lignin / 95% PAN; 10% lignin / 90% PAN; 15% lignin / 85% PAN; and 20% lignin / 80% PAN. Despite the presence of small particles dispersed in the images, likely from the lignin, the analyses by SEM did not give any evidence of phase separation, which is an indication of very good miscibility between the materials involved.

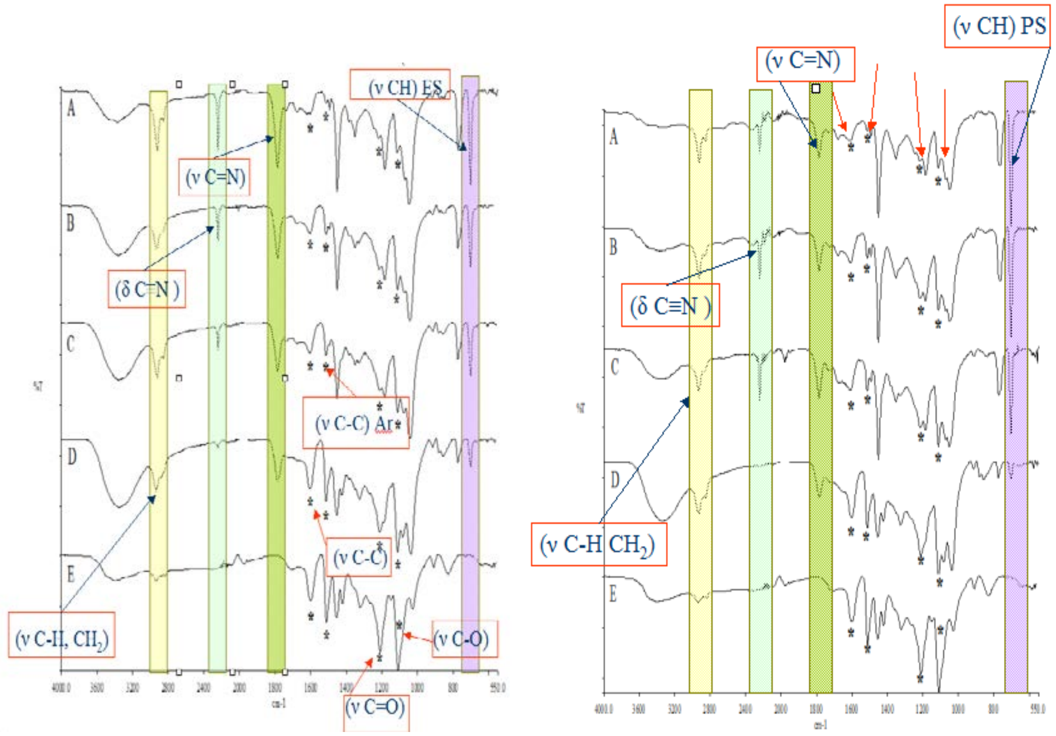


5% lignin / 95% PAN **10% lignin / 90% PAN** **15% lignin / 85% PAN** **20% lignin / 80% PAN**

Figure 3: SEM micrographs from extruded blends with kraft lignin and PAN

The quality of the extruded blend can be compared by their miscibility, where different levels of interaction between PAN and lignin can exist. Lignin is powder filler. Therefore, lower amounts of lignin in the formulation can provide better mixing with PAN. So, it is possible to observe that formulations containing 5% lignin in the composition shows better homogeneity, as no phase separation is observed. The same consideration can be drawn for the blends having 10%, 15% and 20% of kraft lignin, which resulted in a more homogeneous structure, having no observed phase separation. However, from 15% and up of lignin in its composition, the pieces of produced samples of the blends demonstrated, by simple handling the material, to be slightly brittle. At the same way, blends with 20% lignin were evidently the most brittle mixture.

In the FTIR analyses shown in figure 4, the relative transmittances were used to characterize the effects of functional groups of the PAN-co-styrene blended with hardwood lignin (Brazilian eucalyptus) over the analyzed samples. When comparing both FTIR spectra, after (1) and before (2) the extrusion process, they show a very high level of similarity. The assignments of the FTIR analysis spectra represent the formulations of PAN/lignin (A, B, C and D) posted with one analysis done for kraft lignin alone (E). In all spectra it is possible to observe an increase in the absorption (∗) at 1601cm^{-1} (ν C-C), 1516 cm^{-1} (aromatic ring), 1211 cm^{-1} (ν C=O) and 1111 cm^{-1} to (ν C-O), in assignments related to lignin component in blend PAN/lignin.



1) After process extrusion

2) Before process extrusion

Figure 4: 1) and 2): A) 95% PAN + 5% lignin; B) 90% PAN + 10% lignin; C) 85% PAN + 15% lignin; D) 80% PAN + 20% lignin; E) 100% Kraft lignin. The color-highlighted ranges of the plot are relative to PAN-co-styrene. The signals marked with (*) are relative to kraft lignin on the blend.

Also, the assignments relative to PAN in blend PAN-lignin showed the signal intensity decreasing as the amount of lignin in the blend increases, regardless the action of heat during the extrusion process. The assignments like: stretching (ν C-H, CH$_2$), deformation (δ C≡N), stretching (ν C=N) and stretching relative to styrene (ν C-H) from PAN underwent a signal attenuation for higher proportions of lignin in the blend. And, as it would be expected, the assignments relative to kraft lignin on spectra, including stretching (ν C=O), (ν C-O), (ν C-C) and aril (ν C-C), intensified as the amount of lignin increases [10].

So, the results of spectrum analyses suggest that the production of blend PAN-lignin by extrusion process did not cause chemical inter-polymeric reactions among the components of the blend. The results characterize only molecular physical interactions like mechanical anchorage and electrostatic connections.

4. CONCLUSIONS

This work studied the formation of PAN/lignin blends prepared by conventional extrusion process. The materials were analyzed by SEM micrographs and FTIR. By the use of SEM micrographs, it was possible to conclude that blends with composition up to 10% in mass with lignin and 90% with PAN showed good homogeneity, exhibiting no phase separation. Blends having kraft lignin at proportions of 15% and 20% in relation to PAN-co-styrene (10%) exhibited a rough surface aspect, however still without phase separation. When comparing the FTIR spectra from blend samples before and after extrusion, no significant differences were observed. So, based on the performed analyses, no degradation or chemical reactions among the components of the blend have occurred as a result of the heat in which the components were exposed during the extrusion process. It means that the process is appropriate to produce PAN/lignin blends with lignin concentration up to 20%/mass.

ACKNOWLEDGMENTS

This work was main possible due to the support from FIBRIA, CAPES, QUIMLAB and DCTA.

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