NEW MATERIALS ELECTROACTIVE BASED IN THE POLYACRYLONITRILE FIBERS[1]

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Abstracts
New electroactive materials based in the Polyacrylonitrile fibers (PAN) currently are it comes the interest to many researchers in reason of the great application of this polymer in diverse field of the science and industry. Second Schreyer et al (1) the fibers of PAN are of the potential for application as linear actuators and artificial muscles. The objective this work is the synthesis of PAN, doping with $FeCl_3$ and characterization used the techniques spectroscopic of the FTIR, ultraviolet-visible, Mössbauer and x-ray, thermical analysis (DSC, TGA), viscosimeter measurements. The methodology utilized in this work was done in three steps, the first is the polymerization of the acrylonitrile (AN) to polyacrylonitrile for the method described by Sánchez-Soto et al (2). The second step is the heating of this product obtained in first step. The third step was the doping of the PAN with 3 to 10% in mass of $FeCl_3$. The results of characterization of the PAN shows that by x-ray the fibers of PAN it is a semicrystalline polymer with flexible chains in agreement with the obtained by Schreyer et al (1). The spectrum of FTIR and UV-Vis also confirmed the presence of functional groups this polymer and doped with $FeCl_3$ by Mössbauer spectroscopy. It is concluded that the synthesis of polymer it is very interesting and application as artificial muscles will be contribute significantly for development of the news electroactive materials in the field robotic.
Key words: Polyacrilonitrile; Polymer; Artificial muscles; Robotic.

NOVOS MATERIAIS ELETROATIVOS A BASE DE FIBRAS DE POLIACRILONITRILA

Resumo
Novos materiais eletroativos a base de fibras de Poliacrilonitrila (PAN) atualmente vem despertando o interesse de muitos pesquisadores em razão da grande aplicação deste polímero nas diversas áreas da ciência e indústria. Segundo Schreyer e colaboradores (1) as fibras da PAN são de potencial aplicação como atuadores lineares em músculos artificiais. O objetivo deste trabalho é fazer a síntese da PAN, dopagem com $FeCl_3$ e caracterização utilizando as técnicas de espectroscopia infravermelho (FTIR), Ultravioleta-Visível (UV-Vis), Mössbauer, raios-x, análise térmica (DSC e TGA) e medidas de viscosidade. A metodologia utilizada neste trabalho foi feita em três etapas, a primeira é a polimerização da acrilonitrila (AN) em Poliacrilonitrila (PAN) via método descrito por Sánchez-Soto e colaboradores (2). A segunda etapa é o aquecimento deste produto da etapa 1 num frasco fechado a 60°C por 24 h para fazer com que a PAN adquira uma estrutura molecular com cadeia ciclizada. A terceira etapa foi a dopagem da PAN com 3 a 10% em massa de $FeCl_3$. Os resultados da caracterização da PAN mostraram que por difração de raios-x as fibras da PAN são de um polímero semicristalino com cadeias flexíveis em concordância ao obtido por Schreyer e colaboradores (1). Os espectros de FTIR e UV-Vis também confirmaram a presença dos grupos funcionais deste polímero e a dopagem com $FeCl_3$ foi comprovada por espectroscopia Mössbauer. Conclue-se que a síntese deste polímero é muito interessante e sua aplicação como músculo artificial poderá contribuir significativamente para o desenvolvimento de novos materiais eletroativos na área de robótica.
Palavras-chave: Poliacrilonitrila; Polímeros; Músculo artificial; Robótica.

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1 INTRODUCTION

The polymer Polyacrylonitrile (PAN) has a hydrocarbon with nitrile group attached at every other carbon $(-CH_2-CH(CN)-)_n$ that can be produced as gel fibers with elongate and contract when immersed in alkaline and acidic solutions, respectively. PAN fibers have a greater potential for application as linear actuators and artificial muscles than other fibers.[1] The method to prepare chemically activated PAN gel fibers involves two steps: the first step is to anneal the fibers at temperatures between its glass transition temperature (about 110 ºC) and thermal degradation temperature (about 250 ºC) and second step converts remaining nitrile groups on the cross-linked polymer to carboxylic acids by saponification with a strong base.[1,2] In this work, we report the synthesis and characterization of polymer PAN fibers and doped with $FeCl_3$ to generate forces along the length of fibers. The electric properties of PAN fibers prepared were investigated.

2 MATERIAL AND METHODS

The Polymerization of acrylonitrile (AN) to Polyacrylonitrile (PAN) was synthesized using the procedure described by Sánchez-Soto *et al.*[2] where for polymer preparation, was used 3 mL of acrylonitrile (AN, Vetec) and 0.5 wt.% of benzoyl peroxide (Merck) as polymerization initiator were intensively mixed using water as solvent. The product was then heated in a closed flask at 60°C for 24 h to polymerize the AN. The viscosity-average molecular weight of the PAN was found to be 4.4×10^4 in agreement with the literature.[2] PAN fibers were doped by soaking them in range of 3 and 10 wt.% aqueous solution of $FeCl_3$ for 3 h.

3 RESULTS AND DISCUSSION

The X-ray has been used to investigate the structural differences of the PAN samples prepared according to the processing approaches described above. The Figure 1, shows the some differences can be observed between the PAN samples without doped and doped with $FeCl_3$. First of all, an intense peak at 0.5 nm (2θ=17°) characteristic of PAN is detected in the samples, which is more asymmetric when using the solvents. Secondly, the peak at 0.304 nm (2θ=29°), of a much lower of that with doped. According to literature (1,3) the results PAN fibers with linear chains shows a perfect crystal with a diffraction at 2θ=17° which corresponds to (100) planes, and a minor one at 2θ=29° to (101) planes. According to several authors, it is considered that PAN is a semicrystalline polymer with flexible chains. Details of the fiber morphology, in the form of an interplay between crystalline and amorphous regions of this polymer, have an essential effect on their thermomechanical properties.

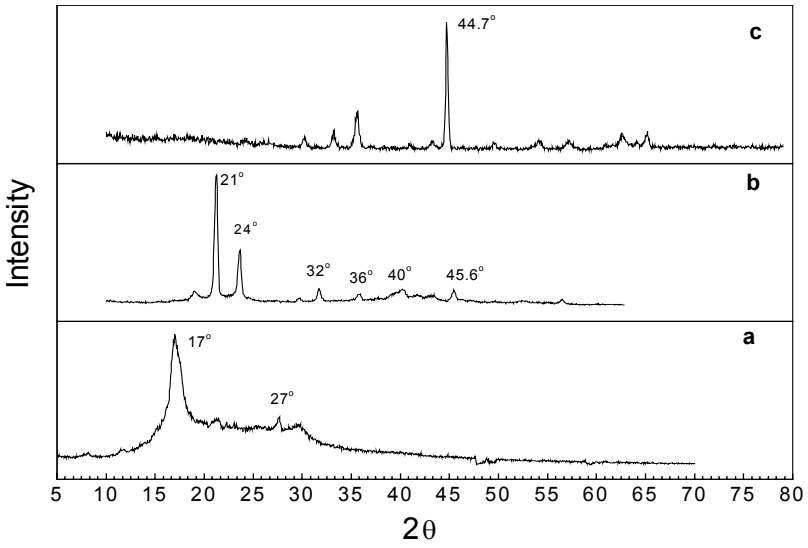

Figure 1 – X-ray of PAN fibers (a) pure (b) 3% $FeCl_3$ (c) 10% $FeCl_3$

The thermal gravimetric analysis (TGA) of PAN samples pure and doped with 3 wt.% of $FeCl_3$ shows that occur a mass loss at around 276 ºC and 357 ºC respectively. Overall, only was 50% of the mass of the sample lost on heating to 910 ºC. The IR spectrum of PAN pure revealed absorption frequencies at 2920 cm^{-1} (C-H streching) and 2244 cm^{-1} (N-H bending and C=N streching) that is characteristic of the polyacrylonitrile macromolecule in agreement with the literature. [4]

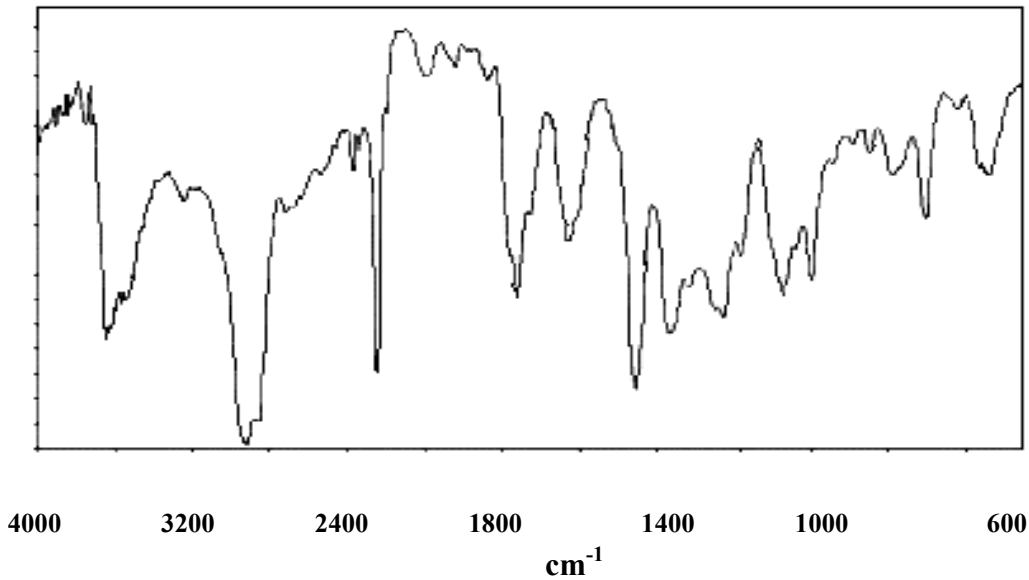

Figure 2 – FTIR of the polyacrylonitrile

The Mössbauer spectroscopy (Figure 3) at 298 K confirmed that doped of PAN with $FeCl_3$ shows a quadrupole splitting and conductivity of 10^{-16} $\Omega \cdot cm^{-1}$.

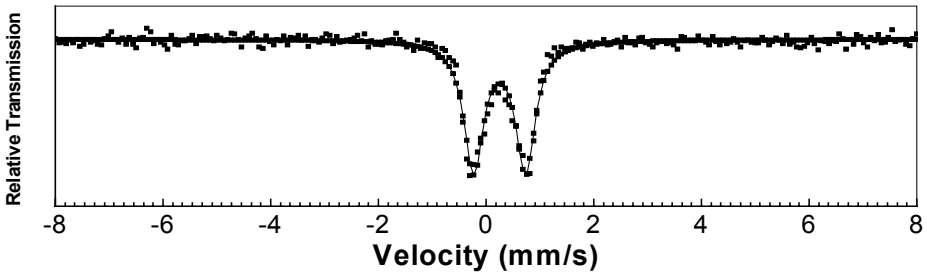

Figure 3 - Mössbauer spectra of the PAN doped with 10% (w/w) of $FeCl_3$

This Mössbauer spectra exhibits a quadrupole as shown in Figure 3 and the fitted parameters are 0.3 mm/s for the isomer shift(δ) that is relative to α-Fe at room temperature and 0.34 mm/s for the quadrupole splitting(Δ). In these Mössbauer spectra of Polyacrylonitrile fibers doped with Fe 10% is identified as a high-spin Fe(III) compound. Kitao et al.[5] studied on $FeCl_3$ doped polythiophene, suggest that production process of $FeCl_4^-$ ions in doping with $FeCl_3$, and following reaction has been proposed: $2FeCl_3 + e^- \rightarrow FeCl_4^- + FeCl_2$.

4 CONCLUSION

The results of the present work reveal that PAN fibers are very interesting and application as artificial muscles will be contribute significantly for development of the news electroactive materials in the field robotic.

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