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Research Article

POLYANILINE: SYNTHESIS, CHARACTERIZATION & CATALYTIC PROPERTIES

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ABSTRACT

In the present work, the polyaniline was prepared by chemical oxidation. Being a conducting polymer, polyaniline has nanostructure properties, good environmental stability and low toxicity. Different forms of PANI, such as pernigraniline base, leucoemeraldine base, and emeraldine base, have various oxidation states and can be found in various forms of crystals, whose conductivity strongly depends on protonation with organic or inorganic acids. Its robust redox properties make it an easy catalyst for various chemical reactions. The feasibility of the catalyst is due to its ease in preparation, handling and stability. The PANI is prepared and characterization was done using various laboratory procedures. These include X-ray diffraction, Fourier transform infrared spectroscopy, UV spectroscopy, and infrared spectroscopy.

Keywords: Chemical oxidative method, Polyaniline, Conducting polymer, Catalyst.

1. INTRODUCTION

A repeating series of units joined together by a covalent bond. This process produces a large-scale molecular material is known as a polymer. Polymeric materials are useful in various industries and their fabrication is done in many ways. They can also be made with dense networking [1]. Conducting polymers [2] such as polyaniline have a large π-electron conjugated structure and generate electrical currents [3]. Alan J. Heeger *et al.* was awarded the 2000 Nobel Prize for his work on the development of conductive polymers.[4] PANI is a homopolymer [5], that has three different oxidation states (Fig. 1). Only emeraldine salt [6] is conducting in nature because of the presence of benzenoid and quinonoid forms at different proportions.

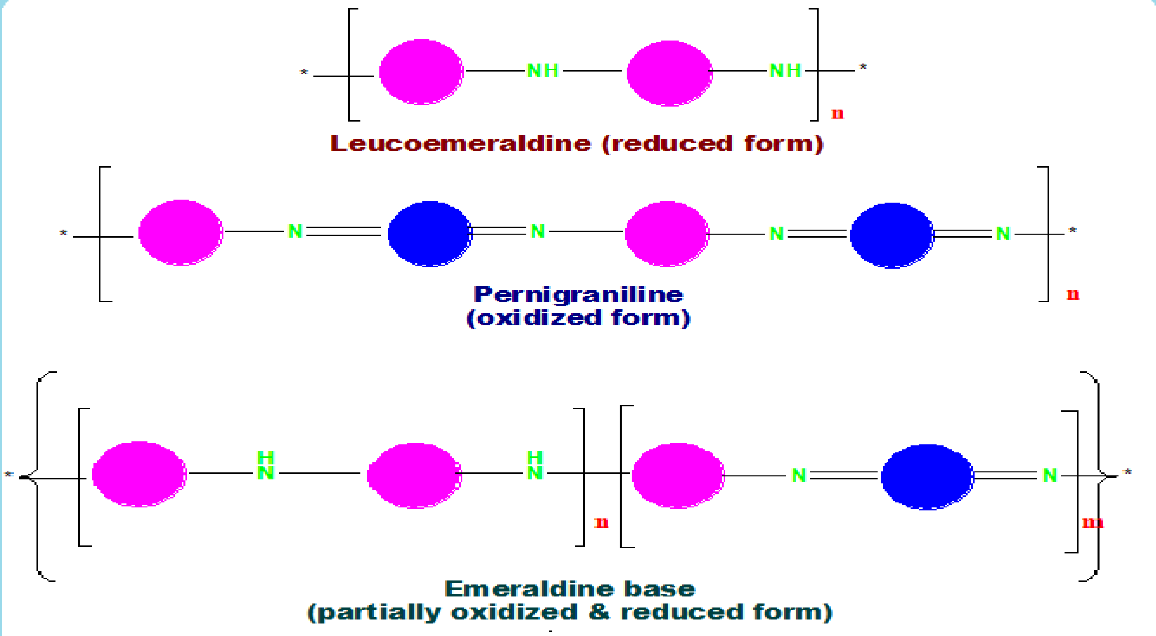


Fig 1: Polyaniline : Structure and Forms

Various synthetic strategies are employed for the synthesis of PANI. However, oxidative polymerization of aniline is the most common method used for the preparation of PANI. [7] Application of polyaniline due to its biocompatibility and low toxicity in various polymeric industries and medical fields. Polyaniline has some disadvantages, such as insolubility and weak processability, however, it can be useful when applying them as the catalyst bed. As the oxidized and reduced form of polyaniline shows different redox states, PANI shows maximum solubility in N-methyl-2-pyrrolidone (NMP) including some polar aprotic solvents like DMSO, DMF and THF. For the conversion of many organic reactions, polymer-supported heterogeneous catalysts are gaining importance. Hence, Polyaniline (PANI) is considered as most useful conducting polymer for catalytical studies and electrical industries due to its redox properties [8] (Fig. 2).

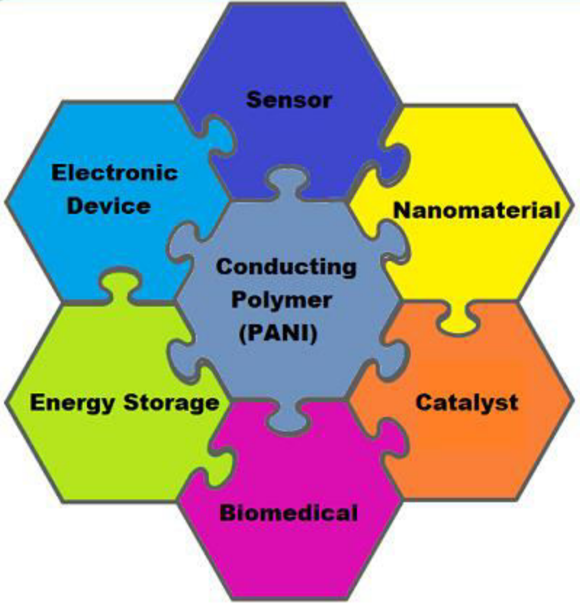


Fig 2: Application of PANI

2. MATERIAL AND METHODS

The DBK precision melting points apparatus was used to measure melting points. Instruments such as Brucker FTIR (KBr) and Shimadzu UV-Visible spectrophotometer were used for Infrared and UV spectra respectively. Bruker 8-D advance X-ray diffractometer, Cu-Kα radiation (λ=1.5405 Å) were used for XRD patterns. The Merck company of high purity (> 99 %) chemicals like aniline, HCl and oxidant ($K_2Cr_2O_7$).

2.1. Experimental: Preparation of Polyaniline

The oxidative polymerization of aniline was carried out using an aqueous 1M HCl solution. The appropriate amount of aniline (0.01 M) is taken, to which 1M HCl was added into the polymerization vessel. Then the vessel was placed on a magnetic stirrer. The reaction was initiated by the addition of 25 ml of 0.01 M $K_2Cr_2O_7$ solution (Fig. 3).

The reaction is highly exothermic; hence the addition rate of oxidant is controlled correctly. After the complete incorporation of an oxidant, this mixture is stirred overnight. The deep green precipitate is formed and filtered, washed with distilled water and diluted solutions of HCl until the filtrate becames colourless and dried at 60°C in the furnace for 5 hrs. The fine green powder of emeraldine salt of PANI was obtained as a product.

The following reactions are proposed during the oxidation of aniline.

The mechanism shown in scheme (1), the oxidizing agent was acidified to produced chromic acid (Eq. 1). The outcome of chromic acid and protonated aniline was a metastable complex [9] (Eq. 2). These unstable complex detached to form the aniline cation radical. (Eq.3). The initiation of radical cation played an essential role in manufacturing the dense polymeric structure of PANI.

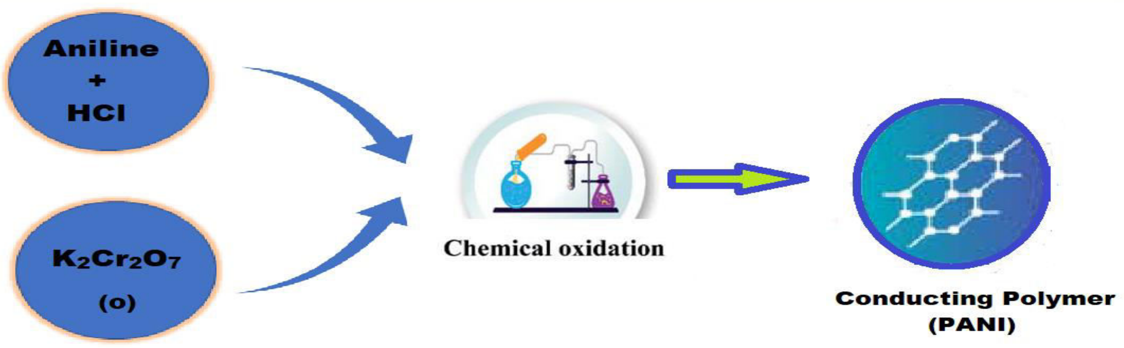
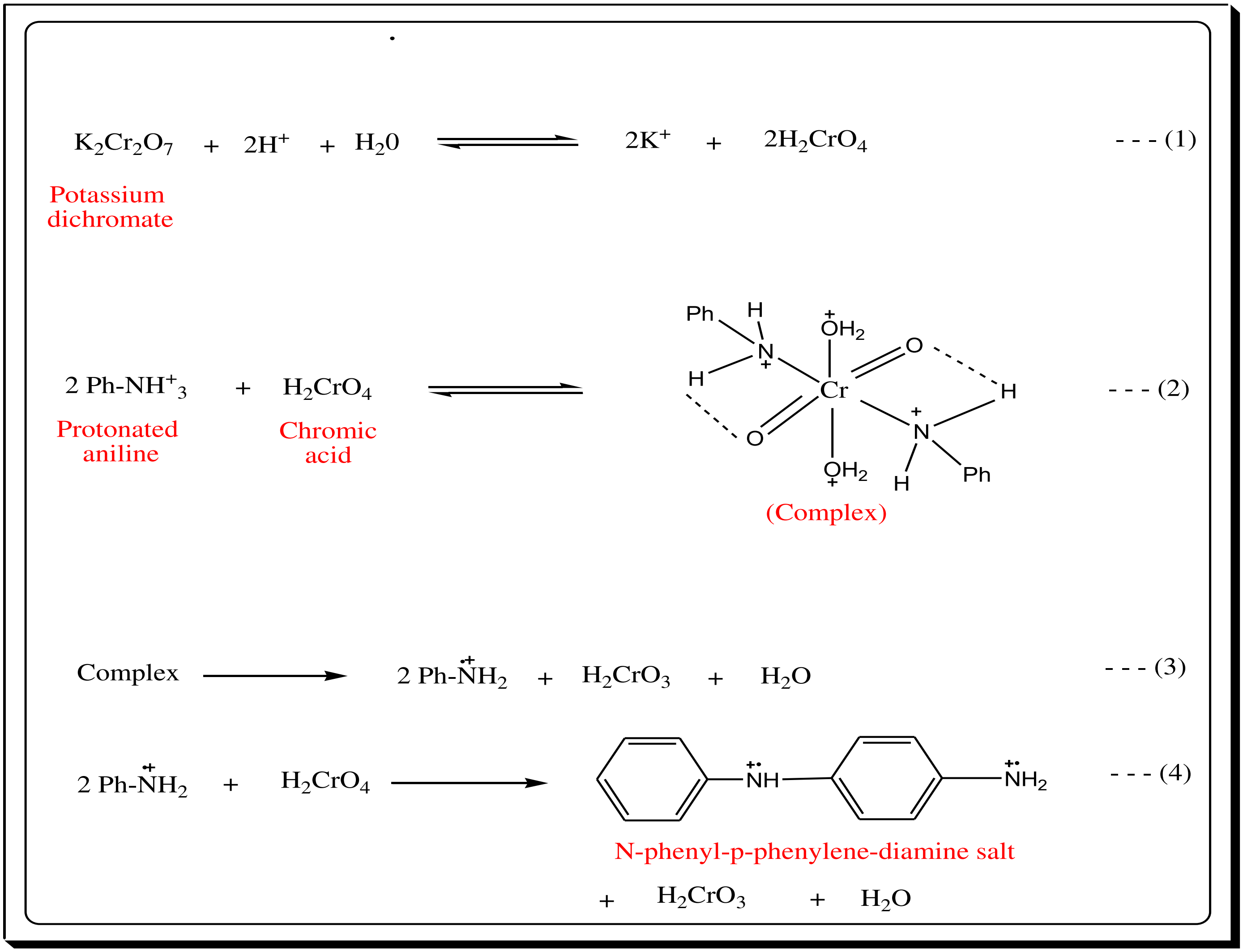


Fig:3 Schematic diagram of chemical polymerization method



Scheme 1: Proposed reaction for the chemical polymerization of aniline

3. RESULTS AND DISCUSSION

3.1. FTIR Analysis

PANI shows characteristic bands as follows (Fig. 4 (A): the N-H stretching band at 3512 cm^{-1} is attributable to N-H stretching mode, the quinoid (C=N) and benzenoid (C=C) rings occur at 1647 cm^{-1} and 1487 cm^{-1}, C-N stretching mode at 460 cm^{-1} and C-H bending vibration at 1296 cm^{-1}, 864 cm^{-1}.

3.2. UV Analysis

PANI shows distinguished UV spectra in Fig. 4 (B): at 333 nm n-π* transitions for the polymeric samples corresponds to aniline. At 640 nm broad bond due to n-π* transitions of quinine-imine clusters.

3.3. XRD Analysis

The polymeric material shows the XRD pattern Fig. 4 (C), the wide peak at around 2θ (25°) which are characteristic of the polyaniline and the small peak is around 2θ (27°) indicates that PANI also exhibits some degree of crystallinity.

3.4. Catalytic Properties

Polymer-supported heterogeneous catalysts [10], doped with active metals are used for variation in organic modifications [11] such as oxidation, dehydrogenation, condensation, Michael [12], Suzuki-Miyaura cross coupling [13] and esterification reactions. The tuneable properties such as environmental-friendly construction, regaining, low-cost, simple plan of action [14] make such heterogeneous catalysts an exciting alternative for conventional and non-regenerable catalysts. Due to the stability in the reaction medium and insolubility in polar protic solvents, PANI- metal complexes can recycle easily (Fig: 5).

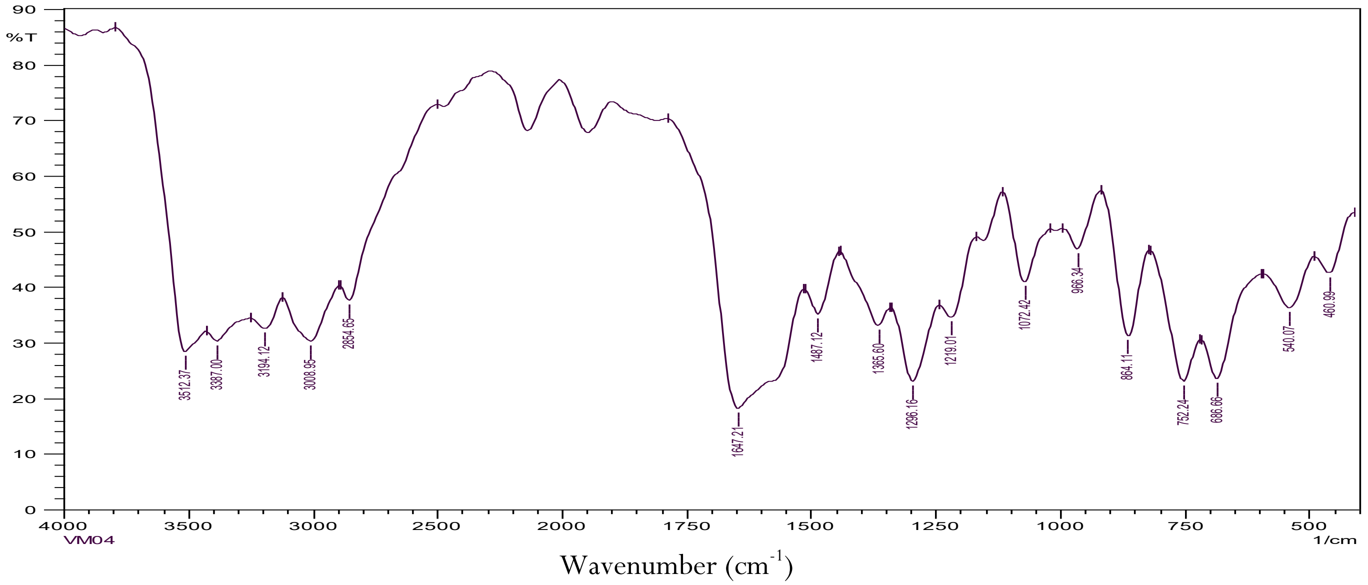


Fig 4(A): FTIR spectra of PANI and

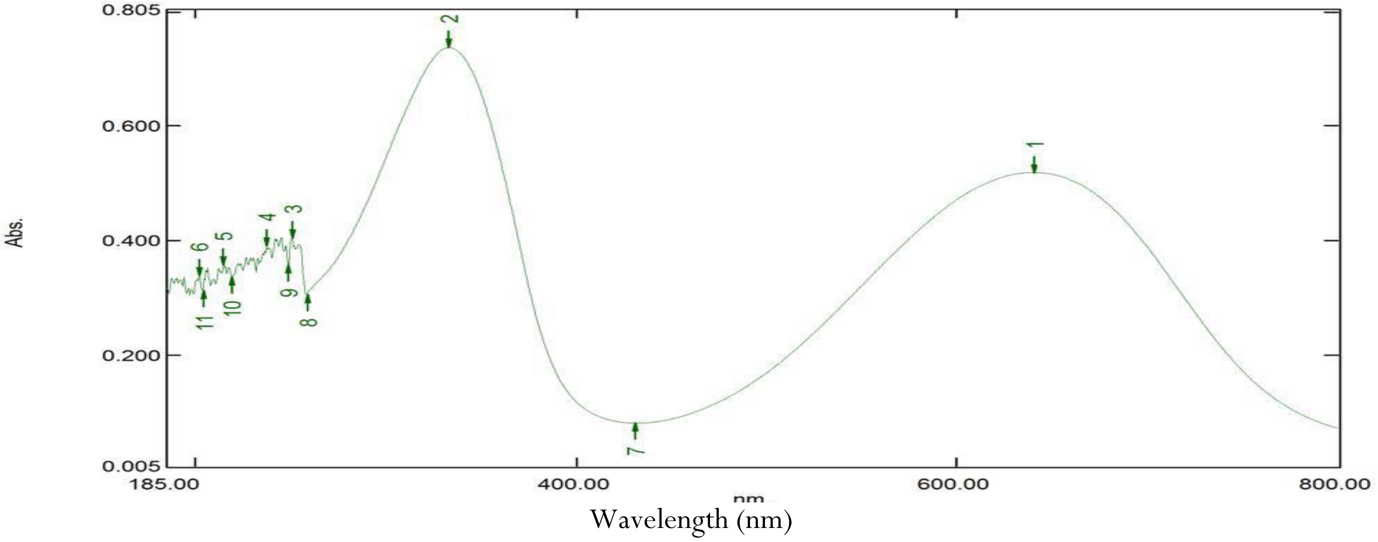


Fig 4(B): UV-Vis spectra of PANI in NMP

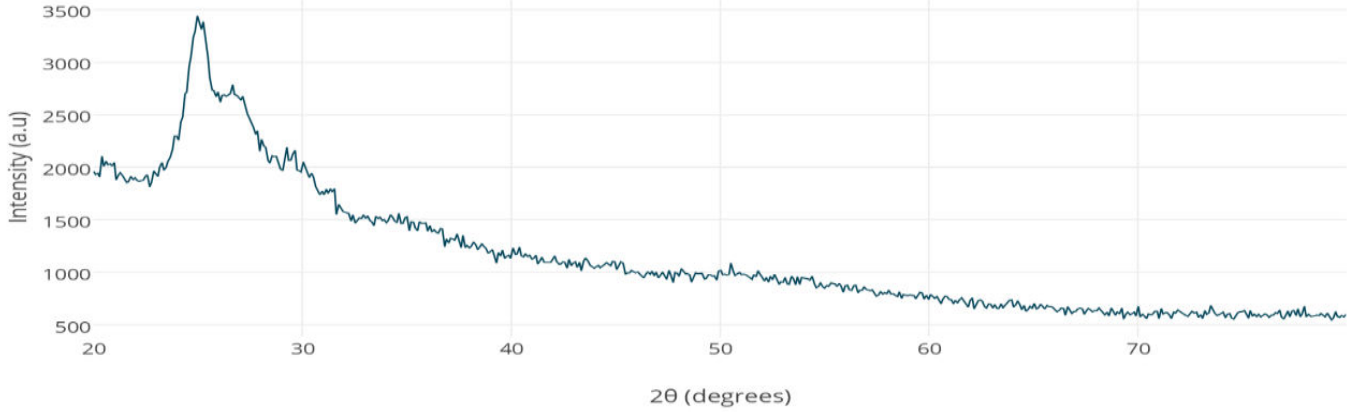


Fig 4(C): XRD pattern of Polyaniline

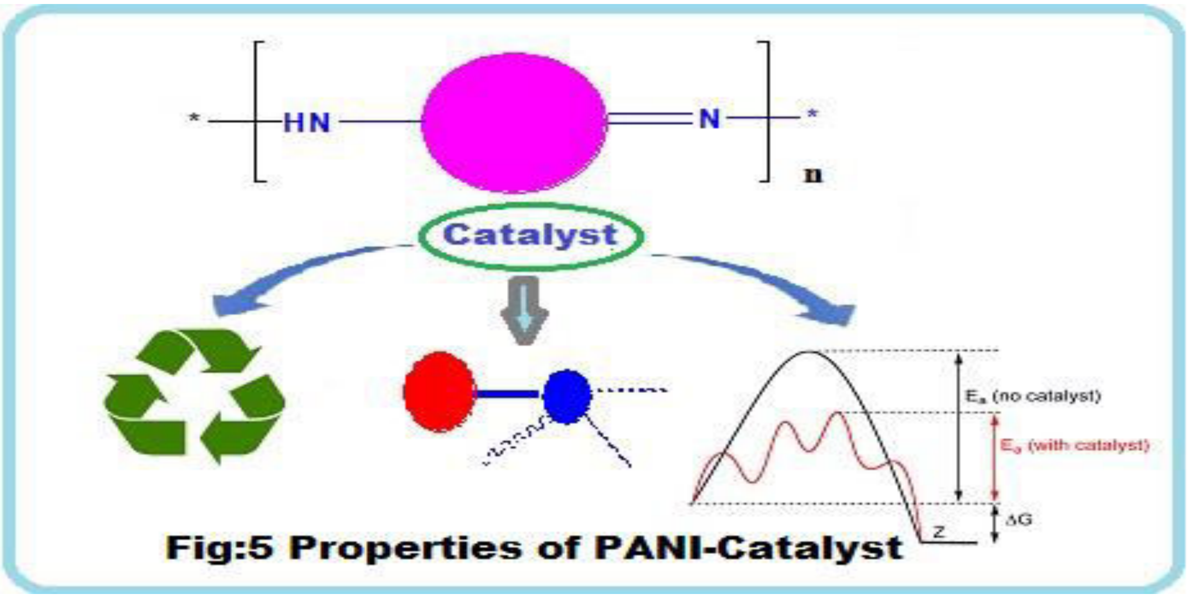


Fig:5 Properties of PANI-Catalyst

4. CONCLUSION

A highly π conjugated system has opened a new synthetic route for the growth of advanced materials. The synthetic procedure with $K_2Cr_2O_7$ as an oxidizing agent empowers polyaniline to show physiochemical effects and facilitate a promising application in the catalyst for various organic transformations. FTIR spectrum showed a quinoid and benzenoid stretching with interchange hydrogen bonds between the imine and amine nitrogen sites on the polymer backbone. A crystallinity in the samples showed by XRD data. The material shows appreciable interest for both productive and economic reasons.

5. ACKNOWLEDGEMENTS

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Conflict of interest

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

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