Optical absorption and morphology of bio-intercalated polyaniline composites

Yesappa L., Niranjana M., Sharanappa Chapi, Archana K., Raghu S., Devendrappa H.*

Department of Physics, Mangalore University, Mangalagangothri, 574199, India

*Corresponding author: Tel: (+91)082-42888707; E-mail: dehu2010@gmail.com

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Abstract

Bio-intercalation based Polyaniline (PANI)-Aloe vera (AV) with Lithium Perchlorate ($LiClO_4$) composites has been synthesized by In-situ chemical reaction method. The composite was employed characterizations with help of Fourier Transform Infrared (FT-IR) Spectroscopy and Scanning Electron Microscopy (SEM) to know the chemical interaction and morphology of the composites. From SEM result it was noticed that morphology became changes significantly with reduce porosity. The Ultra Violet Absorption (UV-Vis) study shows that absorption increases as well as maximum peak shifts and PAL10 red shifts in visible region at 615nm. These results manifest that PANI-AV/$LiClO_4$ (PAL) composites are the promising materials for solar cell, LED's and electrical applications.

Keywords: Conducting polymer, polyaniline composites, FT-IR, morphology, UV-Vis absorption.

Introduction

Conducting polymers (CPs) and their composites have been intensively studied due to uniqueness and various potential applications. Among the various available conducting polymers like polythiophene (PT), polyaniline (PANI), polypyrrole (PPy), poly (3, 4–ethylenedioxythiophene) (PEDOT), and poly (p-phenylene vinylene) (PPV) etc. Polyaniline (PANI) has paid considerable attention owing to its good electrical conductivity, simple synthesis processabiliy, environmental stability, and good electrochemical properties. The conjugated π-electron system is suitable for fabricating composites with various binders and substrates **[1]**. The preparation of PANI composite received great development owing to the excellent work by Huang and Kaner *et al.* **[2, 3]**. Ability of PANI to exist in various oxidation states and protonation degree ranging from the most reduced leucoemeraldine form to the fully oxidized pernigraniline form makes it a unique and interesting polymeric material **[4]**.

PANI is generally more complex with respect to other conducting polymers; it depends on both the pH value and protonic acids, the emeraldine salt form exhibits the high conducting properties **[5]**. The lithium perchlorate ($LiClO_4$) is the most widely used electrode material in lithium batteries technologies. Such material undergoes oxidation and reduction reactions involving release and loading of lithium cations. The conducting Polyaniline (PANI) is a suitable material as a matrix of such composite material because of its easy processabiliy, special doping mechanism, low cost, and high environmental stability. Electrical conductivity studies of LiCoO2/PANI composite materials done in **[6]**. *Aloe vera* is the most available biocomponent in the medical field and we try to combine it with polymeric material.

This paper presents the synthesis of the PANI-AV/$LiClO_4$ composite and subsequently adding the bio component AV and study its different properties were due to effect of $LiClO_4$. The composite structure improves the optical properties with more absorption in visible region and decreases the porosity in the morphology with increase in concentration of salt to 10%, these material is promising candidate for solar cells, LED's, super capacitor applications, and also battery applications.

Experimental Methods

Materials

Aniline (Sigma-Aldrich, 99.5% purity) distilled under reduced pressure, Lithium perchlorate ($LiClO_4$) (mol wt.106.4 g/mol, Sigma-Aldrich USA, 95.0% purity) is used as received. Ammonium persulfate $(NH_4)_2S_2O_8$ (mol wt. 228.20 g/mol Merck, 95.58% purity), Hydrochloric acid (mol wt. 36.46, 35-38% purity), and all other chemicals used were of analytical reagent (AR) grade. *Aloe vera* is extracted from natural plant.

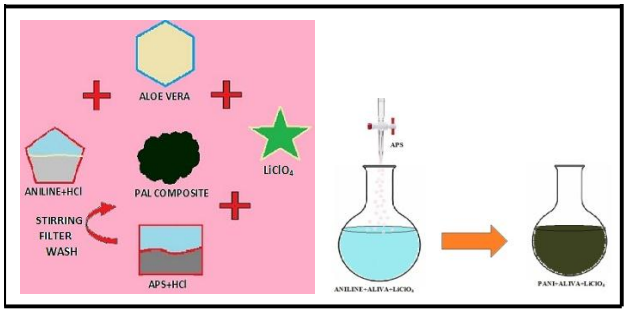
Synthesis of polyaniline

The conducting PANI was synthesized by the chemical oxidation method by taking 4.5 ml of aniline in 100ml of 1M HCl in a round bottom flask adding 2.8gm of APS in 100ml of 1M HCl through the burette under the ice bath

with constant stirring still the dark green precipitation formed and further proceeded as reported in **[7]**.

Synthesis of PAL composites

The preparation of PANI-*Aloe vera*: 5% of $LiClO_4$ and PANI-*Aloe vera*: 10% of $LiClO_4$ as appropriate ratios and coded as PAL-5 and PAL-10, respectively. These composites synthesized by oxidative chemical reaction method as above mentioned. The synthesis and titration process of PANI and its composites are clearly shown in the **Scheme 1**.



Scheme 1: Schematic representation of PANI-*Aloe vera*/$LiClO_4$ composite.

Characterization methods

The chemical changes of the PANI and PAL composites were analyzed by Fourier transform infrared spectrometer at spectral range of 1600-600 cm^{-1} (FT-IR, Alpha Bruker). The surface morphology has been observed using a Sigma Zeiss scanning electron microscope (SEM). All images were acquired using an operating voltage of 15 kV with a magnification of 100X in order to limit the charging effects. The optical absorbance (A) of the samples was measured as function of wavelength (λ) in range from 200-1000nm by using computerized Lambda-35 UV-Vis spectrophotometer (Perkin-Elmer).

Results and discussion

FT-IR spectra analysis

The FT-IR spectrum of PANI and PANI/AV/$LiClO_4$ composite is shown in **Fig. 1**. The characteristic bands in the FTIR spectra of PANI composite occur at 1350, 1262, 1190, and 836cm^{-1} **[8]**. The PANI band at 1350cm^{-1} is assigned the C–N stretching mode of benzenoid units (in-plane bending modes) have shifts to 1352 and 1354 cm^{-1} for PAL5, PAL10 composites. The peaks 1262 of PANI have shifts to 1266,1270cm^{-1} for PAL5, PAL10 composites and 1190 cm^{-1} is shifts to 1193cm^{-1} in PAL10 due to vibrational band of nitrogen quinone band stretching (C=N stretching -N =quinoid=N-).

The PANI peak at 836cm^{-1} has shifts to 842cm^{-1} in PAL10 is attributed to C–H for the benzenoid unit. The formation of new peaks at 1506 and 1508cm^{-1} in PAL5 and PAL10 composites are corresponds to C=C stretching of benzenoid ring **[9]**. The shifting peaks and arising new peaks confirms the interaction in the PAL composites.

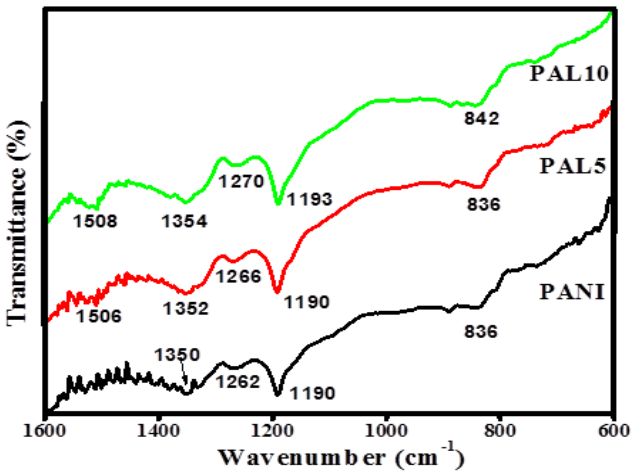


Fig. 1. FT-IR spectra of PANI, PAL5, and PAL10 composite.

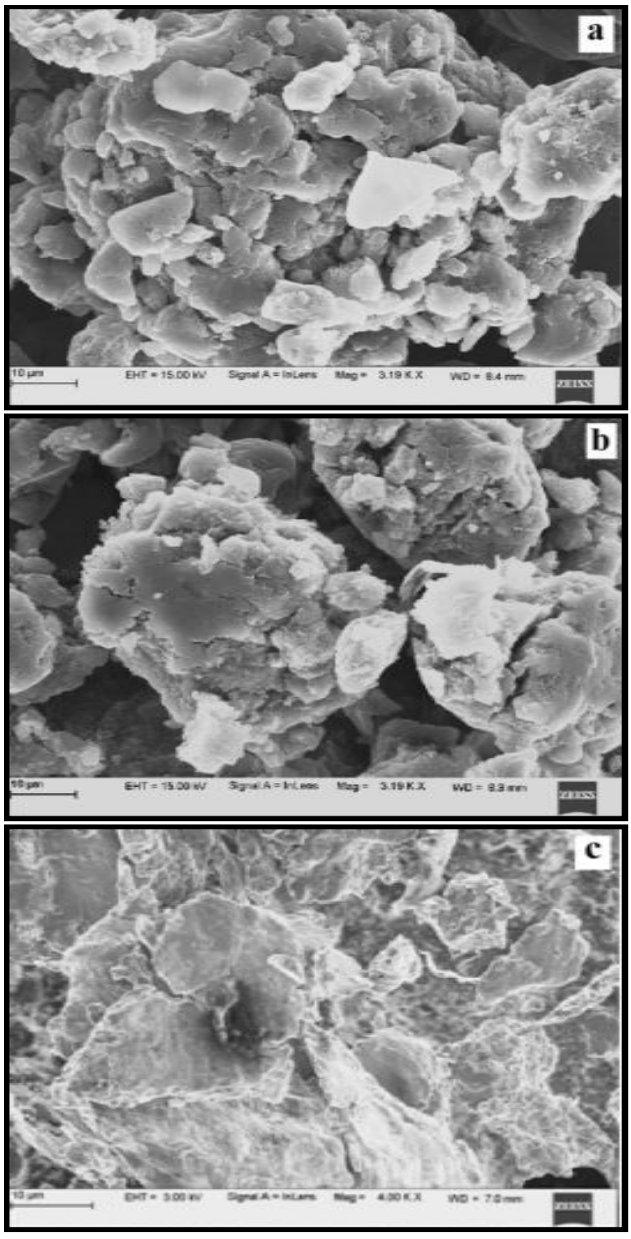


Fig. 2. SEM images of a) PANI, b) PAL5, and c) PAL 10 composites.

SEM analysis

The surface morphology of the PANI alter with increasing in $LiClO_4$ component wt% and becomes smooth due to the presence of the AV in the PAL composites as given in **Fig. 2(a-c)**. The PANI shows the amorphous nature with aggregation of grains is well interconnected morphology with highly agglomerated irregular flakes shape.

The morphology of PAL 5 composite shows with flat surface due to the lithium perchlorate with spherical granules in shape. The additives effect is more clearly observed in the PAL10 composite as shown in **Fig. 2(c)**. It is seen that increase in the homogeneity in shape. From the SEM result, it was noticed that morphology became changes significantly with increasing composite concentration.

UV-Visible spectrometer

Fig. 3 shows UV–visible spectra of (a) PANI, (b) PAL5, and (c) PAL10. The optical characteristic peaks of the PANI are occurred at 370, 517 and 905nm. The peak at 370nm is assigned to the π–π* transition associated with the π electrons in the benzene rings of the PANI. This peak was shifted towards higher wavelength 381nm in PAL5 and lower wavelength side to 328nm in PAL10. For PAL5 exhibits the red shifts i.e. peak at 517nm has shifts to 592nm and at 615nm for 10 wt% of salt with very high intensity as shown in **Fig. 2(c)**, it is attributed to the molecular exciton from the highest occupied molecular orbital (HOMO) of the benzenoid rings to the lowest unoccupied molecular orbital (LUMO) quinoid rings. This represents the existence of polaron and protonation of the polymer as reported in **[10]**. The peak of PANI at 905nm shows a free carrier tail confirmed the presence of conducting emeraldine salt of the host polymer **[11]**.

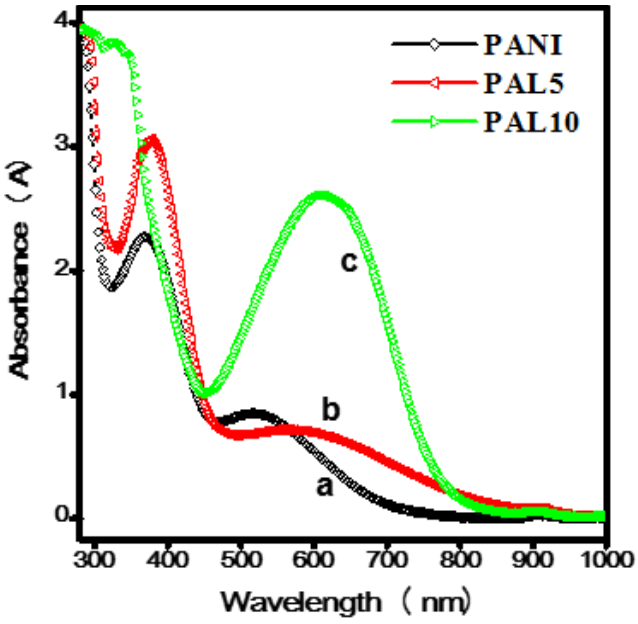


Fig. 3: UV-Visible spectra of a) PANI, b) PAL5, and c) PAL 10 composite.

These changes are due to the addition of lithium perchlorate and AV in the composite. The Ultra Violet Absorption study shows that absorption increases as well as peak shifts with concentration. UV spectra of PAL composite exhibits the peaks around the 270-290nm with high intensity are reveals the presence of AV due to inter-band transition of core electrons of Li^+ ions **[12]**. The PAL10 composite shows high absorption and more peak shifts also confirms from FT-IR result.

Conclusions

We have synthesized the Polyaniline (PANI)-AV/$LiClO_4$ composites by In-situ chemical reaction method. The FT-IR result confirms that composite proper chemical interaction and characteristic peaks shifting to higher wave numbers revealed the effectiveness of composite. The surface morphology of the composite was varied and observed the decrease in the porosity with clear and compact shaped morphology indicates that conductivity increases by increasing the lithium perchlorate amount to 10 wt% in the composite. The Ultra Violet Absorption study shows that absorption increases as well as maximum peak shifts in PAL10 composite. These results manifest that PANI-AV/$LiClO_4$ composite with 10 wt% of salt are the promising materials for solar cells, LED's, and super capacitor applications.

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Author's contributions

Conceived the plan: Yesappa L., Devendrappa H.; Performed the experiments: Yesappa L., Niranjana M., Devendrappa H.; Data analysis: Yesappa L., Niranjana M., Sharanappa Chapi, Devendrappa H.; Wrote the paper: Yesappa L., Niranjana M., Archana K., Raghu S., Devendrappa H. Authors have no competing financial interests.

Supporting information

Supporting informations are available from VBRI Press.

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