Transmittance and Reflectance Spectra of Doped-Polyanisidine-Derived Film in the Visible Light Region

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Abstract. Polyanisidine (PAnis) powder was synthesized using a standard procedure. It was doped with Hydrochloric (HCl) and Perchloric (HClO₄) Acids. The air-dried PAnis powder was then diluted using Dimethyl Formamide (DMF) as solvent and was spread out in a SiOₓ transparent glass substrate. An amorphous and semi-transparent film was fabricated seen in a polarizing microscope. The spectral analysis was carried out in the visible region from 400 nm to 700 nm. For HCl-doped sample, the high intensity region in the transmittance spectra occurred at the green portion while the high intensity region for the reflectance spectra was seen at the violet portion. Lastly, for the HClO₄-doped sample, the peak intensities are at 536 nm and 516 nm for the transmittance and the reflectance spectra, respectively.

1. Introduction

Since the emergence of intrinsically conducting polymers (ICPs), the problem has always been on the processing of conventional polymers. [1] For recent years, advances have been made in the area of solution processing to pave way in the processing of transparent, highly conducting films and coatings. With these, there opens a big potential for industrial applications ranging from electrostatic dissipation to electrochromic displays.[2] Thus, optical analysis is desired to probe polyanisidine properties for specific applications.

Doping changes the structure and property of prepared materials and therefore will have a direct effect on the their optical properties. Visual inspection of the Polyanisidine (Panis) film shows difference in color depending whether light is transmitted or reflected from the doped film. With this, the concern of the paper is to plot and to compare the reflectance versus wavelength spectra and transmittance versus wavelength spectra of the film.

Results in this study is valuable for future researches to account for the difference between the observed colors. Observation in the visible light region is vital in tuning the optical properties of films. Also, this paper aims to synthesize Panis powder and to process the product to fabricate film.
2. Methodology
2.1.1. Sample Preparation. Panis was synthesized using standard chemical method same as that of Polyaniline which is more commonly prepared [3]. The oxidizing agent used to polymerize Anisidine is Ammonium Peroxydisulfate (APS). Two samples were prepared with hydrochloric (HCl) acid and perchloric (HClO₄) acid as dopants. The precipitate was air-dried for a day.

To prepare the film, the precipitate was then dissolved in Dimethyl Formamide (DMF), which is a known organic solvent. The solution was spread out onto a Silicon Dioxide (SiOₓ) transparent glass substrate. The film was observed under a polarizing microscope to determine its structure.

2.1.2. Spectral Measurements. A reflectance spectrometer was used to determine the reflectance of film on a SiOₓ substrate. The measurement was done at an angle 45° with respect to the normal of the film. The set-up was modified for transmittance in which the sensor was placed behind the sample. Both the reflectance and transmittance were done from 400 nm to 700 nm wavelength. Also, the reflectance and transmittance spectra of the substrate were obtained. These were accounted for in determining the transmittance and reflectance of the film alone. The spectra of the film were normalized to unity to observe the difference in the behaviour of the graph.

3. Results and Discussions
3.1.1. Panis Film. The Panis film is successfully prepared and the film is fabricated. Visual inspection shows a semi-transparent green film. Studying the structure of the film under a polarizing microscope shows that the film is amorphous. In which under crossed-polars, the image remains extinct as the stage is rotated.

3.1.2. Spectral Analysis. The general form of the graph does not change when the spectra with glass slide is incorporated compared to when the glass slide is eliminated. The glass slide only lowers the intensity but does not change the behaviour of the spectra. This means that the glass slide does not contribute any significant changes in the colour of the film. With the elimination of the spectra of the substrate, the optical property of the film alone can be investigated.

![Spectra of Panis-HCl Doped](image)

**Figure 1.** Transmittance and reflectance of Panis film doped with HCl showing a change in color from green to violet.
Figure 1 shows the difference in the highest intensity peaks of the transmittance and reflectance of Panis film doped with HCl. The high intensity region for the transmittance is at the 500nm to 550 nm which corresponds to the green portion of the light spectra. On the other hand, the high intensity region for the reflectance has occurrence at 400nm to 450 nm region corresponding to the violet part of the light spectra.

![Spectra of Panis-HClO4 Doped](image)

**Figure 2.** Transmittance and reflectance of Panis film doped with HClO₄ showing a change in color from higher wavelength to a lower wavelength of green.

Doping decreases the resistance of the film. Highly oxidizing acids such as HCl and HClO₄ leads lessen more the resistance of the film. Figure 2 shows the peaks of the transmittance and reflectance spectra of Panis film doped with HClO₄ which occured both at the green region. The peak in the graph for transmittance is at 536 nm while the reflectance’s peak is at 516 nm. It is noteworthy saying that the change in color for the HCl-doped sample is larger than the difference for that of HClO₄-doped sample.

The results for the transmittance are similar to the behaviour of the transmittance spectra for polyaniline films and coatings where in general the transmitted color defined by the graph is green. A part from varying the coatings to tune the optical property of the polymer, varying the dopant changes the transmittance spectra of the films. These have direct changes in the surface conductivities of the samples. [4, 5]

On the other hand, the reflectance behaviour of Panis films can be seen similar with the polyaniline camporsulphonic (Pani-CS) acid-doped samples and polypyrrole hexafluorophosphate (PF₆), p-toluensulfonate (TsO), and sulphated polyhydroxyether (S-PHE)-doped samples Ultraviolet-Visible (UV-vis) light spectra.[6] For metallic conductors, reflectance approaches unity at high wavelength.[7] The whole band of spectrum is necessary to observe this. In the visible light region, the trends of the reflectance plots show transition to metallic conductivity since a different behaviour is seen.
4. Conclusions
Polyanisidine powders doped with HCl and HClO₄ were synthesized. A visually semi-transparent film of green color was fabricated. It was observed that there was a difference in the highest intensity regions for the HCl-doped sample while a difference in the highest peaks was noted for the HClO₄-doped sample.

References

[1] T. A. Skotheim (ed.), Handbook on Conducting Polymers, Vols. 1 and 2, Marcel and Dekker, Inc. Newy York, 1986
[2] V. G. Kulkarni, Transparent Conductive Coatings: *Handbook on Conducting Polymers*. 1059. Marcel and Dekker, Inc. Newy York, 1986
[3] J. Stejskal ad R. G. Gilbert. *Polyaniline-IUPAC: Technical Report*. Pure Applied Chemistry 74, 5, 857-867.
[4] V. G. Kulkarni, J. C. Campbell, and W. R. Mathew, Transparent Conductive Coatings, *Synthetic Metals*. 55-57:3780-3785 (1993).
[5] Y. Cao, P. Smith, and A. J. Heeger, Counter-ion induced processability of conducting polyaniline, *Synthetic Metals*. 55-57:3514-3519 (1993).
[6] R. S. Kohlman and Arthur J. Epstein. Insulator-Metal Transition and IHomogeneous Metallic State in Conducting Polymers: *Handbook on Conducting Polymers*. 99, 103. Marcel Dekker Inc., New York, 1998.
[7] H. Ehrenreich and H. R. Phillipp, *Phys. Rev*. 128:1622 (1962).