IOSR Journal Of Applied Physics (IOSR-JAP)
e-ISSN: 2278-4861.Volume 12, Issue 3 Ser. I (May – June 2020), PP 17-24
www.Iosrjournals.Org

Effect of pH on the optical-Absorption of polyaniline Carboxymethyl Cellulose thin Films.

Anene, C. R, and Nwokoye, A.O.C.
Department of Physics and Industrial Physics
Nnamdi Azikiwe University, Awka, Anambra State.

In the present research, we report the experimental deposition of polyaniline carboxymethyl cellulose (PANI CMC) thin film by in situ deposition technique. The PANI CMC thin films were further immersed in a buffer solution of different pH values. The optical absorption measurement was carried out in order to estimate the optical properties and bandgap energy using a UV-Visible spectrophotometer. It was observed that with variation in pH, the optical bandgap energy was between 2.80 eV to 2.48eV. The absorption peaks are evident around 302nm, 600-620nm, and around 790-800nm. This confirms the polaron and bipolaron band transition in Polyaniline. The PANI CMC thin-film composite has high transmittance 75% -98%. Poor reflectance of less than 13%, high refractive index, high optical conductivity, and low values of extinction coefficient.

Keywords: *UV-VIS, pH values, Absorbance, bandgap energy.*

Date of Submission: 02-05-2020 Date of Acceptance: 16-05-2020

I. Introduction

Polyaniline is one of the oldest known conducting polymers. First discovered in the 19th century as "aniline black" (Syed *and* Dinesan 1991; Genies *et al.*, 1990), It has been the most studied conducting polymer closely followed by polypyrrole (Stejskal *et al.*, 2010) It was later found to be electrically conductive in nature and many researchers began to closely examine the properties of this material. The conductivity of PANI can be changed by doping and spans a very wide range ($<10^{-12}$ to 10^5 S cm^{-1}) depending on the level of doping space (Rao and Sathyanarayana 2001). The changes in physicochemical properties of PANI occurring in response to various stimuli are used in various applications, e.g. in sensors, actuators, optoelectronics, electrode materials, in electro-catalysis, in solar energy conversion (Stejskal and Gibert 2002).In view of this, thin films of conducting polymers including PANI have been studied by several researchers, because of their special electrical properties, their considerable thermal stability, and oxidation resistance. The establishment of the physical properties of PANI reflecting the conditions of preparation is thus of fundamental importance (HungVan Hoang, 2006).

In the past few years, several novel methodologies have been developed for the preparation of nanostructured PANI in the form of dispersions, nanowires, nanofibers, and nanotubes (Stejskal, et al., 2010, Gupta, and Miura, N. 2005, MacDiarmid, et al., 1985. Thus, the PANI and their composite have served as an impetus for many studies on conductive blends to obtain a wide range of conductivities for various potential applicants. Thus, by blending PANI with the other polymers of fillers, new materials possessing improved processability, flexibility, and controllable conductivity can be obtained (Kelly, et al., 2013, Anderson, et al., 1991, Chang, et al., 2012) Cellulose along with other natural biopolymers has gained considerable research interest among material science because of its environmentally attractive origin and properties like renewability, biocompatibility, biodegradability, abundance, high specific strength, and non-abrasiveness during processing. (Ravikirianet al., 2014, Guo et al., 2013). Consequently, we considered Carboxymethyl cellulose (CMC) to be composited with Polyaniline (PANI). Moreover, CMC is a water-soluble polysaccharide cellulosic ether which can be extracted from the fibrous tissue of plants (Basavaraja et al., 2013) and can readily interact with host molecules to form a composite system due to the presence of carboxymethyl groups with composite electric charges in it and so would greatly contribute to synergistic effects in a composite system, thus offering scope for tailoring their properties (Guo et al 2015, Abdel- Galil et al 2014, El- sayed and El Gamal 2015).

In this paper, we present our investigation of the effect of pH on the optical properties (UV- Visible) of the thin film of polyaniline carboxymethyl cellulose deposited on a glass slide by in situ polymerization technique.

II. Experimental Procedure

Materials AR grade aniline and carboxymethyl cellulose used in this work were procured from Merch. The potassium dichromate ($K_2Cr_2O_2$) was from the Kernel, concentrated Hydrochronic acid from BBH Oceanic Chemical Nigeria limited. Hydrogen sulfate (H_2SO_4) was from Sigma Aldrich. The glycerol and sodium laurel sulfate (SLS) from Avondale laboratories Ltd. All were used without further purification. Distilled water was used for all experiments.

Formulation of Inks

Ink Solution A

The beaker was first rinsed with distilled water and 50ml of water was added into the beaker, 2.469M of Aniline was weighed using an electronic balance and put in the beaker, 6.515M of glycerol, 0,02M of sodium lauryl sulfate (SLS), 2.465M of H_2SO_4 and 0.567M of CMC were equally poured into the same beaker also and stirred using the magnetic stirrer for few seconds. Water was added to make up 150 ml this gives solution A.

Ink Solution B

The beaker was first rinsed with distilled water and 50ml of water was added into the beaker, 0.876M of potassium dichromate was measured and put in the beaker. 0.52M of glycerol was equally measured and put in the beaker, this was stirred for a few seconds using the magnetic stirrer. This result gives solution B.

Preparation of Polyaniline Carboxymethyl Cellulose (PANI CMC) thin film

The PANI CMC- the thin film was synthesized by in situ polymerization technique. Five slides were cleaned by rinsing with distilled water and allowed to dry. 3 drops of stock A was dropped on each slide, followed by a drop of stock B and allowed to stand for 40 seconds, without rinsing the five slides were immersed into a beaker each in different pH buffer solutions of 10,6,4,2, and 1 respectively. This was allowed to stand for 60 seconds and quickly taken each straight to the UV-VIS spectrophotometer for characterization. The absorbance spectra data were obtained from UV 752 UV-VIS spectrophotometer. From the absorbance, various other parameters which include: Optical band gap, Transmittance, Refractive index, Coefficient of absorption, optical conductivity, and dielectric constant were derived.

III. Results and Discussion

Figure 1 shows the absorption spectra of PANI thin films recorded over a wavelength range of 230 nm to 1100nm - Vis spectrophotometer. The absorbance (A) of all the samples as a function of wavelength was plotted to observe the possible transitions at different wavelengths.

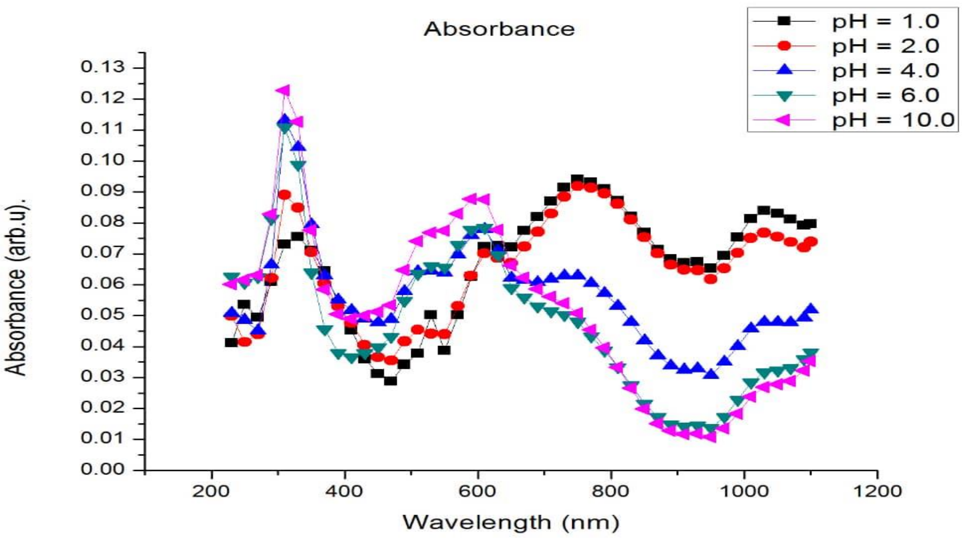

Figure 1: Absorbance values of PANI CMC at different pH values versus wavelength

The PANI CMC was observed to exhibit poor absorption of electromagnetic radiation throughout the UV/VIS region of the electromagnetic spectrum. Absorption peaks are evident around 320 nm, 600 – 620 nm, and around 790 – 800 nm. The absorption peak exhibited by the films around 320 can be attributed to the electron transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) corresponding to the $\pi \rightarrow \pi^*$ electronic transition (Kofi et al., 2016, Kulkarni *et al*., 2004, Kulkarni *et al*., 2013, Zeng *et al*., 2015 and Tissera *et al*., 2018). The peak at 600 – 620 nm is as a result of the quinonoid ring transition, which represents the charge transfer from the HOMO of the benzenoid ring to the LUMO of the quinonoid ring (Zeng *et al*., 2015) and the peak at about 800 nm corresponds to the conducting phase of the polyaniline representing the polaron and bipolaron band transition respectively. These results agree with previous works of Kulkarni *et al*., (2004); Kulkarni *et al*., (2012) and Tissera *et al*., (2018) (Basavaraja 2012)

Figure 2 shows the bandgap energy spectra of the film. From the figure, it is observed that the bandgap energy increases from 2.40eV to 2.80eV as the pH increases, with a drop to 2.78eV at pH 10. The bandgap of 2.40eV - 2.80eV corresponds to the emission of polymer in the solid-state demonstrating the optical properties of the polymer (Amer *et al.*,2015, Anene and Nwokoye 2019) This may be useful for finding applications in electrochromic and optoelectronic devices (Sharma *et al.*,2013*).*

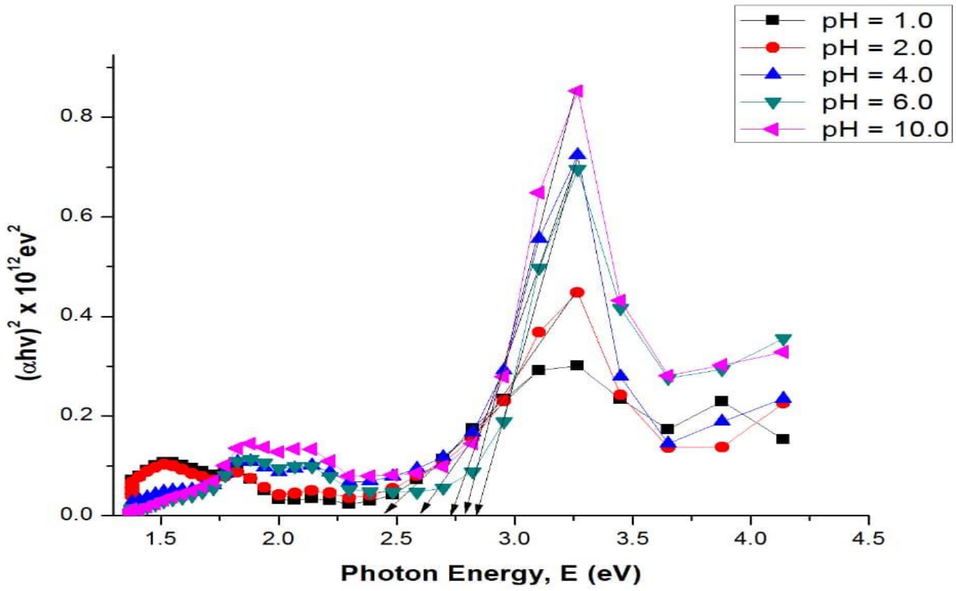

Figure 2: Plot of $(\alpha hv)^2$ versus photon energy for pH variations of PANI CMC samples

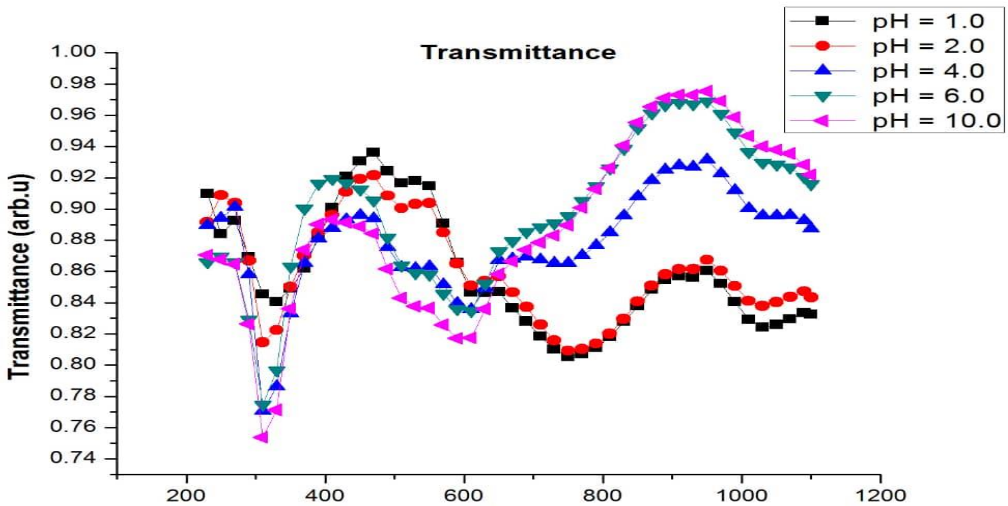

Figure 3: Transmission spectra for PANI CMC samples at different pH Variation.

Figure 3 shows the transmission spectra of the films. From Figure 3, the range of transmittance is between 75% and 98% for all cases of pH variations. High transmittance of about 80% for polymeric materials has previously been reported by Alias et al., (2013). The general high transmission displayed by the films in all cases of investigation suggests its suitability in optoelectronics applications. **Figures 4 shows** the reflection values of the PANI CMC samples were plotted against wavelength for different pH variations.

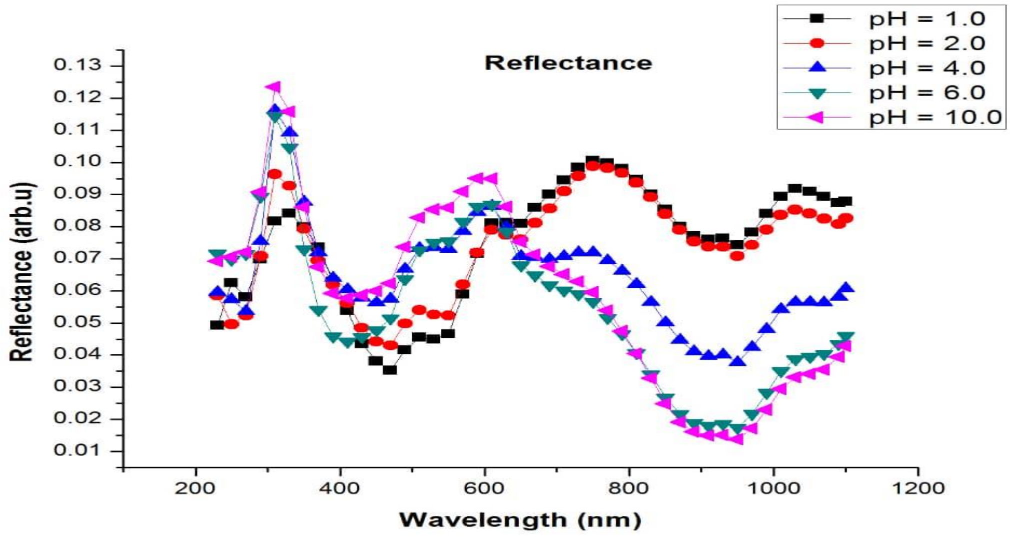

Figure 4: Reflectance plots of PANI CMC samples against wavelength for pH variation

The reflectance spectra exhibited poor reflection of radiation (less than 13%) throughout the UV-VIS region of the electromagnetic spectrum. The reflectance value ranges from 0.08 (8%) to 0.128 (12.8%). The films at different deposition time exhibited poor reflectance of electromagnetic radiation. **Figure 5** shows the absorption coefficient values plotted against photon energy. The absorption coefficient values increased as the pH increases. Absorption coefficient values are in the order of 10^6. The absorption coefficient is between 0.18 to 0.28.

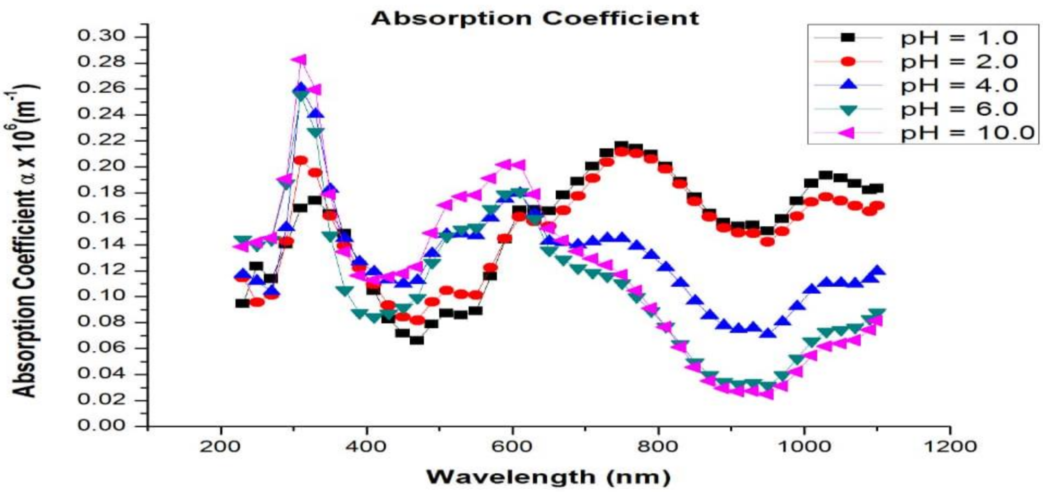

Figure 5: Absorption coefficient values of P3 samples versus wavelength.

Figure 6 shows the refractive index of the material plotted against photon energy for different pH variations. The refractive index (R.I.) values of the material were observed to substantially as the pH values are increased from 1second to 10 seconds in the visible region. The refractive index was between 1.82 and 2.10. In all cases of time variations, the material had higher R.I. values in the visible region. High refractive index values suggest the material's usefulness in optoelectronics applications.

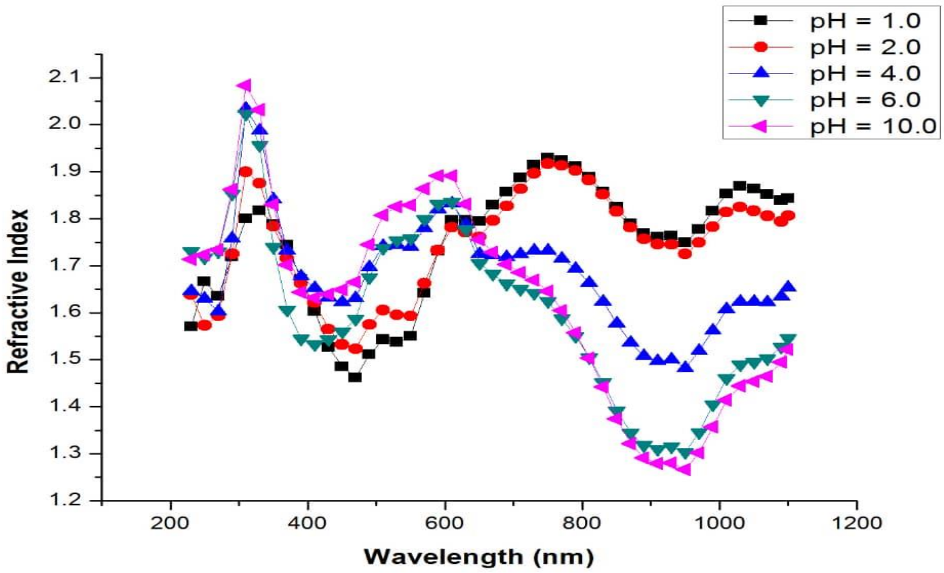

Figure 6: Plot of refractive index versus wavelength for PANI CMC samples at different pH variations

Figure 7 shows the optical conductivity of the PANI CMC material plotted against wavelength.

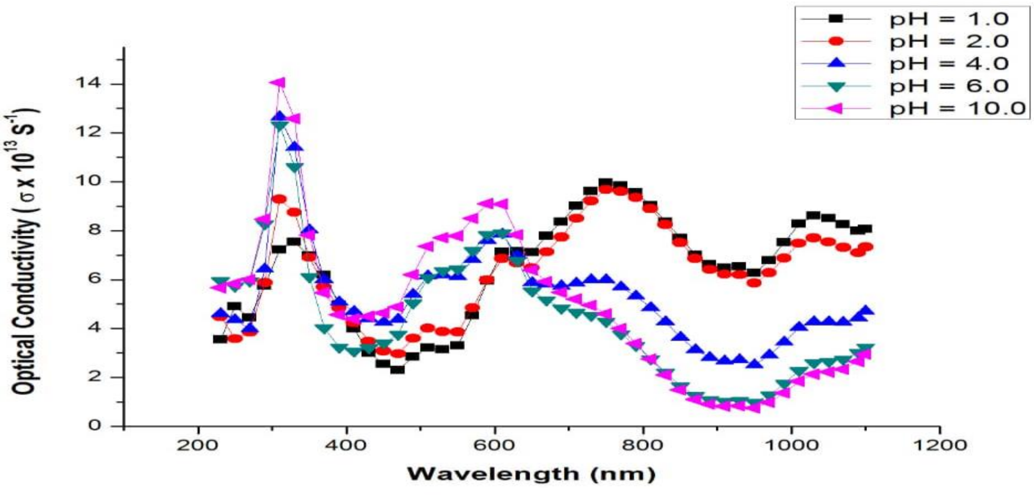

Figure 7: Plot of optical conductivity versus wavelength PANI CMC samples at different pH variations

Figure 7 shows the optical conductivity of the material was observed to increase substantially as the pH values increases. The optical conductivity of the samples is of the order of 10^{13} in the range of 7 to 14 S^{-1}. **Figure 8**shows the plot of the extinction coefficient against wavelength. From figure 8 extinction coefficient was from 0.005 to 0.007. The material was observed to have very low values of the extinction coefficient. Low values of the extinction coefficient confirm high transparency of the material (Amatalo, 2014, Anene and Nwokoye 2019).

The material possessed very high optical conductivity, which gives the material credence in optical and optoelectronic applications.

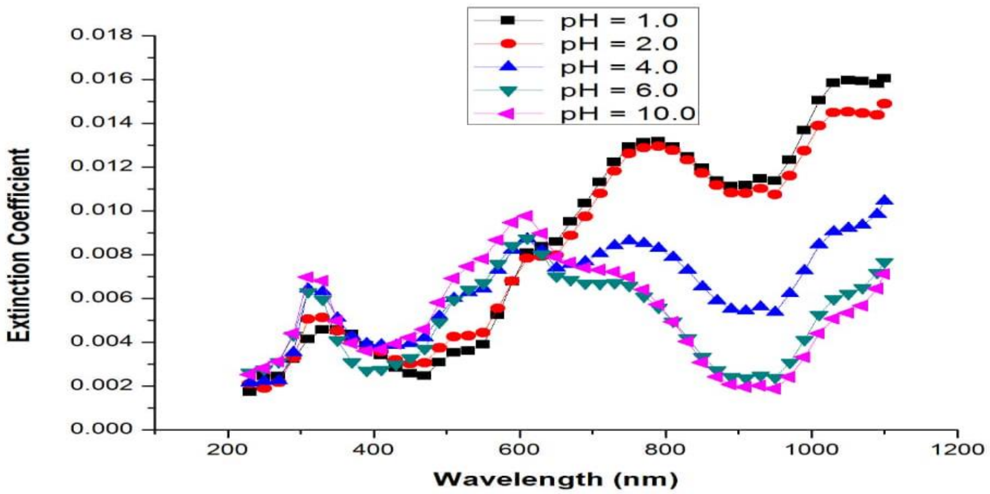

Figure 8: Plot of extinction coefficient values versus wavelength for different pH samples variation.

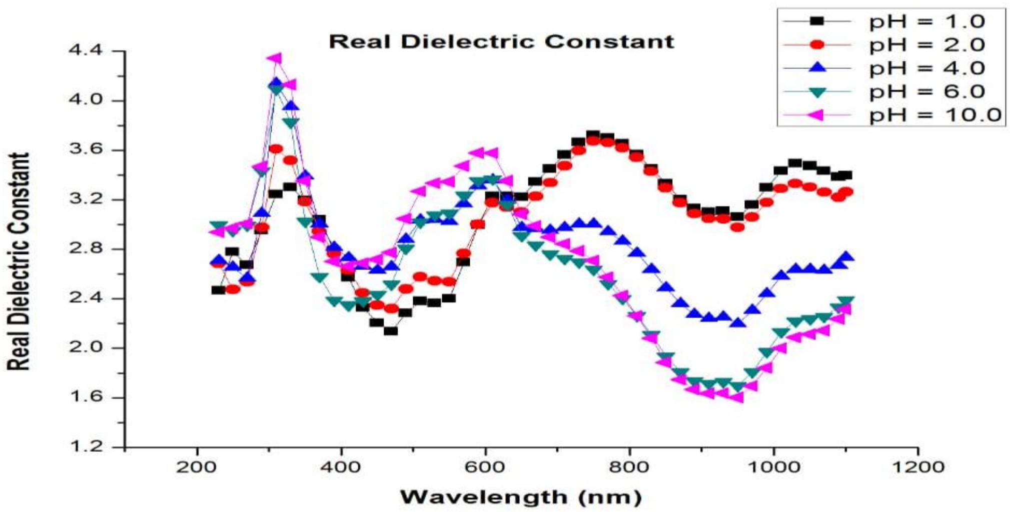

Figure 9: The plot of the real dielectric constant against wavelength for pH variation of PANI CMC samples

Figure 9, the range of real dielectric constant was in the range of 3.25 to 4.40 for the different pH variations. Figure 9 indicates that the real dielectric constant values increased in response to an increase in pH variation. Thus, real dielectric constant values were observed to depend on the pH variations. **Figure 10** shows the imaginary dielectric constant of the PANI CMC plotted against wavelength for all different pH variation

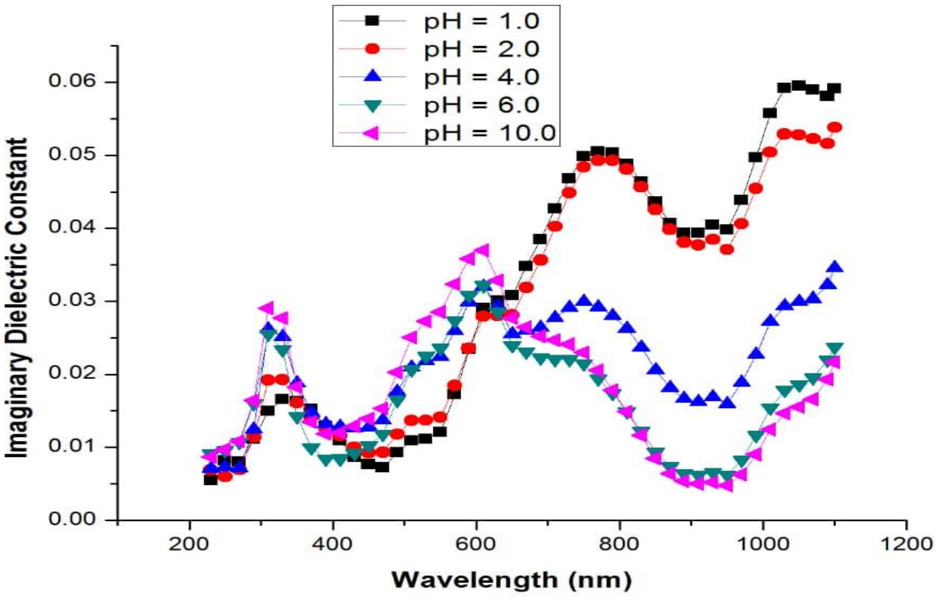

Figure 10: The plot of the imaginary dielectric constant against wavelength for pH variations.

From Figure 10 the values for imaginary dielectric constant were between 0.015 and 0. 003. The imaginary dielectric constant values increase with increasing pH variations. The films had a very low imaginary dielectric constant.

IV. Conclusion

The thin-film of PANI CMC composite was prepared by an in situ process and characterized for optical absorbance. From which other optical properties were calculated. It was observed that with variation in pH solution the optical band gap energy values were between 2.48 eV to 2.78eV. The PANI CMC was observed to exhibit poor absorption of electromagnetic radiation throughout the UV/VIS region of the electromagnetic spectrum. The PANI CMC thin-film composite has high transmittance 75% -98%, Poor reflectance less than 13%, high refractive index, high optical conductivity, and low values of extinction coefficient. The present study on the preparation method of PANI CMC thin-film composite is facile and cost-effective. This may find potential applications in nanoelectronics like pH sensors.

Reference

[1]. Alias A. N., Zabidi Z. M., Ali A.M.M., Harun, M. K. (2013). Optical Characterization and Properties of Polymeric Materials for Optoelectronic and Photonic Applications, International Journal of Applied Science and Technology, 3(5), 11- 37.

[2]. Amatalo, I. (2014). Fabrication and Characterization of Al/ZnSE Film Schottky diode. Unpublished M.Sc. Thesis, Department of Physics, Kenyatta University, Kenya.

[3]. Amer N. J; Kamarulazizi I. and Nasser, M.A. (2015). Synthesis and characterization of the thin film of conductive polymer (PANI) for optoelectronic device application. A paper presented at the International Conference on Nano-electronic Technology Devices on materials by the American Institute of Physics. AIP conference proceeding. 1733, 020021-1-020020-7 Dio 10.1063/1. 4948838.

[4]. Anderson, M.R. Mattes, B.R.; Reiss, H.Kaner, R.B. Conjugated polymer films for gas separations. Science 1991, 252, 1412–1415.

[5]. Anene, C.R and Nwokoye, A.O.C (2019) Synthesis and characterization of polyaniline carboxymethyl cellulose (PANI CMC) for optoelectronic device application, Advanced Material Science,4,1-5.

[6]. Basavaraj, C., Kim, J.K., Huh, D.S. (2013). Characterization and temperature-dependent conductivity of polyaniline nanocomposites encapsulating gold nanoparticles on the surface of carboxymethyl cellulose Mater Sci Eng. B 178:167-173.

[7]. Bamfo-Asante, A.A, Isaac Nkrumah, Mark Paal, and K. Singh, Effect of Deposition and Annealing Temperatures on Optical Band Gap of Sno2 Thin Films Deposited on Glass Substrate by Chemical Vapor Deposition (CVD) method. (2015) International Journal of Advanced Research in Engineering and Technology, 6(4)9–16.

[8]. Chang, C.-H.; Huang, T.-C.; Peng, C.-W.; Yeh, T.-C.; Lu, H.-I.; Hung, W.-I.; Weng, C.-J.; Yang, T.-I.; Yeh, J.-M. Novel anticorrosion coatings prepared from polyaniline/graphene composites. Carbon 2012, 50, 5044–5051

[9]. El-Sayed, A.M., EL-Gamal, S. (2015). Synthesis and investigation of the electrical and dielectric properties of CO3O4| (CMC + PVA) nanocomposite films. Journal of Polymer Resources, 22,1-12

[10]. Genies, E. M., Boyle, A., Lepkowski, M., and Tsintavis, C., (1990) Polyaniline: a historical survey. International Conference Synthetic Metals,36(2),139–182

[11]. Guo, B. Glavas, L. Andertsson, A, (2013). Biodegradable and electrical conducting polymer for biomedical applications. Prog Polymer Sci 38: 1263-1268.

[12]. Gupta, V.; Miura, N. Large-Area network of polyaniline nanowires prepared by the potentiation deposition process. Electrochemical. Commun. 2005, 7, 995 999.

[13]. Hung V.H. (2006). Electrochemical Synthesis of Novel Polyaniline-Montmorillonite Nanocomposites and Corrosion Protection of Steel. Unpublished M.Sc thesis, Department of Electrochemistry, Chemnitz University of Technology, Vietnam
[14]. Kelly, F.M.; Meunier, L.; Cochrane, C.; Koncar, V. Polyaniline: Application as solid-state electrochromic in a flexible textile display. Displays 2013, 34, 1–7.
[15]. Kulkami, M. V., Sonali, D.N., Jalinder, D., Ambelear, S. and Bharat, B.U. (2012) inkjet printed conducting polyaniline base flexible humidity sensor. The 14^{th} international meeting on chemical sensors 1112-1115.
[16]. Kulkarni, M. V., Viswanath, A.K., Marimuthu, R and Seth, T. (2004) Synthesis and characterization of polyaniline doped with organic acids' J. Polym. Sci. A 42, 2043-2049
[17]. . Kofi Owusu-Sekyere, Isaac Nkrumah, R. K. Nkum, and K.Singh. A Study of Optical Absorption of Polyaniline thin films prepared by Chemical Bath Deposition (CBD) Method. (2016) International Journal of Advanced Research in Engineering and Technology, 7(2),109–117.
[18]. Macdiarmid, A.G.; Mu, S.-L.; Somasiri, N.L.D.; Wu, W. Electrochemical characteristics of "polyaniline" cathodes and anodes in aqueous electrolytes. Mol. Cryst. Liq. Cryst. 1985, 121, 187–190.
[19]. Rao, P. S., Sathyanarayana, D. N. (2001). Advanced Functional Molecules and Polymers, H. S. Nalwa (ed.), Gordon and Breach, Tokyo,
[20]. Ravikiran, Y.T., Kotresh, S., Vijayakumari, S.C., Thomas, S. Liquid, (2014). Petroleum gas sensing performance of polyaniline carboxymethyl cellulose composite at room temperature. Current Applied Physics 14, 960-964.
[21]. Sharma I.D, Saino, P.U, and Sharm V.K (2013).Structural, optical, morphological, and electrical characteristics of polyaniline for device applications. Indian Journal of engineering and material sciences 20, 145-149.
[22]. Stejskal, J., and Gilbert, R. G. (2002). Polyaniline: Preparation of a conducting polymer (IUPAC technical report), Pure and applied chemistry, 74(5), 857–868.
[23]. Stejskal, J., Sapurina, I., and Trchova, M., (2010). Polyaniline Nanostructures and the Role of Aniline Oligomers in Their Formation. Progress in Polymer Science, 35, 1420-1482.
[24]. Stejskal, J.; Sapurina, I.; Trchová, M. Polyaniline nanostructures and the role of aniline oligomers in their formation. Prog. Polym. Sci. 2010, 35, 1420 1481
[25]. Sun, Y. M. Diarmid and A. J. Epstein, J. (1990) Chem. Soc. Chem.Commun., 7,529.
[26]. Syed, A.A., and Dinesan, M.K. (1991). Review: Polyaniline-A novel polymeric material. Talanta,815–837.
[27]. Tissera, N. D., Wijesena, R. N., Rathnayake, S., De Silva, R. M., De Silva, K.M. N. (2018) Heterogeneous in situ polymerization of polyaniline (PANI) nanofibers on cotton textiles. Carbohydr Polym.186, 35-44.
[28]. Zeng, F., Zongyi, Q, Banglei, L, Tao., L., Liu, N., Meifang, Z.(2015) Polyaniline nanostructures tuning with oxidants in the interfacial polymerization system. Progress in Natural Science: Materials International 25 512–519

Anene, C. R, et. al "Effect of phontheoptical-Absorption of polyaniline Carboxymethyl Cellulosethin Films." *IOSR Journal of Applied Physics (IOSR-JAP)*, 12(3), 2020, pp. 17-24.