Nanoscale Reports

3(1) (2020) 39-44

DOI:10.26524.nr.3.8

RESEARCH ARTICLE

OPEN ACCESS

Influence of Annealing Temperature on Optical, Chemical and Particle size Properties of Polyaniline Nanomaterial

N. Dhachanamoorthi[1], S. Haripriya[1]

Abstract

Polyaniline is a representative conducting polymer because of its high electrical conductivity in doped state and it's used in various fields of science and engineering because of its unique characteristics. Polymers are playing a dominant role in many areas such as material sciences, textile industries and chemical industries. Monomers of aniline are combined together to form a polymer of polyaniline by chemical oxidative polymerization method. The process of synthesis includes 1.5 M of aniline (C_6H_5N) as main reagent which causes chemical reaction, Sulfuric acid (H_2SO_4) as a dopant which alters its original electric and optical properties and Ammonium Peroxydisulfate (APS) as an oxidant which has the ability to oxidize and accept electrons. The synthesized nanoparticles are subjected to heating process at two different temperatures (20˚C and 40˚C). The prepared polymer material is characterized by UV-Visible Spectroscopy, Fourier Transform Infra-Red Spectroscopy, Particle Size Analyzer and antibacterial activity. The electron transition from ground state to excited state was revealed by UV-Vis Spectroscopy. Polymeric materials are identified using FTIR spectroscopy and it also exhibits the chemical bonds and structure of the sample. Particle Size Analyzer represents the mean size of the polyaniline sample. The overwhelming potential application of polyaniline includes manufacturing of circuit board, corrosion resistance, and fabrication of smart textiles.

Keywords: Material sciences, Ammonium Persulfate, FTIR spectroscopy, UV-Vis Spectroscopy, Antibacterial activity.

Author Affiliation: [1]Department of Physics, Vellalar College for Women, Erode-12, Tamil Nadu, India.

Corresponding Author: N. Dhachanamoorthi. Department of Physics, Vellalar College for Women, Erode, Tamil Nadu, India, Email: dhachu83@gmail.com

How to cite this article: Dhachanamoorthi, S. Haripriya, Influence of Annealing Temperature on Optical, Chemical and Particle size Properties of Polyaniline Nanomaterial. *Nanoscale Reports* 3(1), 39-44. Retrieved from http://nr.eleyon.org/index.php/nr/article/view/8

Source of support: Nil

Conflict of interest: None.

Received: 18 March 2020 **Revised:** 25 April 2020 **Accepted:** 27 April 2020

1. Introduction

For the past few decades, special attention has been paid for the synthesis of synthetic materials like polyaniline, pyrrole, thiophene etc., Polyaniline has its application in antistatic coating, electrode material for batteries and condensers, microelectronics, corrosion resistance due to its specific properties.[1] These conducting polymer possess different oxidation states. They are thermally stable and hence they are determined by regular structure of polymer chains.[2,3] In the oxidative polymerization method, oxidation takes place and the formation of charge carriers takes place in polymer. Some conducting polymers including polyaniline have shown that they also possess semiconducting properties.[4] PANI has also been electrochemical oxidative polymerization method or by chemical polymerization method. PANI exhibits highly reversible redox behavior and considered as advanced polymer in the device fabrication like industrial sensors.[5,6] This type of conducting materials are directed in the field of sensors developing, manufacturing of artificial noses and electronic tongues which has its application in detecting chemical vapors and gases. The electronic structure and electronic properties can be controlled by both oxidation and protonation.[7] It also possesses electrochemical behavior and can be easily synthesized. The typical PANI consists of chemically stable -NH- group attached by phenyl rings on both sides. It is also to be noted that the three oxidation states of PANI has different physical and chemical properties.[8] These conducting polymers are characterized by electronic properties of semiconductors and they exhibit a conjugated structure of alternate single and double bonds.[9] In this present study, PANI was synthesized by chemical oxidative polymerization method and it can be dissolved in various acids like H_2SO_4 which can be used as a dopant for the synthesis mechanism. The as-prepared samples were characterized by number of techniques and the results are analyzed.

2. Experimental Procedure

Chemical oxidative Polymerisation method is employed here for the synthesis of polyaniline. In this method, sulphuric acid is used as a dopant to alter its original electric and optical properties and ammonium peroxydisulfate is used as an oxidant which oxidizes. In this process, 1.5 M (13.6955 ml) of aniline is taken in a conical flask and 100ml of distilled water is added in it. It is then mixed by placing it in a magnetic stirrer for 10 minutes at 600 rpm. After the completion of 10 minutes, 5.3304 ml of sulphuric acid is added to the above mixture and stirred for 30 minutes. Then 2.8525 g of ammonium peroxydisulfate is mixed with 25 ml of distilled water and the solution is added drop by drop to the mixture using the additional flask. The change of colour is noticed. The colour of the mixture was changed from golden yellow to brown colour and then to green colour which shows that polymerization was taking place. After the addition of APS solution, the resulting mixture was allowed to stirred for 24 hours. Then after the completion of stirring process, precipitate is obtained and it is filtered through the Mann filter paper and it is washed over 20 ml of acetone and 25 ml of ammonia for removing the impurities. The obtained precipitate is dried for various temperatures like 60˚ C, 200˚ C, 300˚ C, 400˚ C in the vacuum. After the drying process, the fine powder was obtained by grinding it in agate mortar and four different samples were obtained.

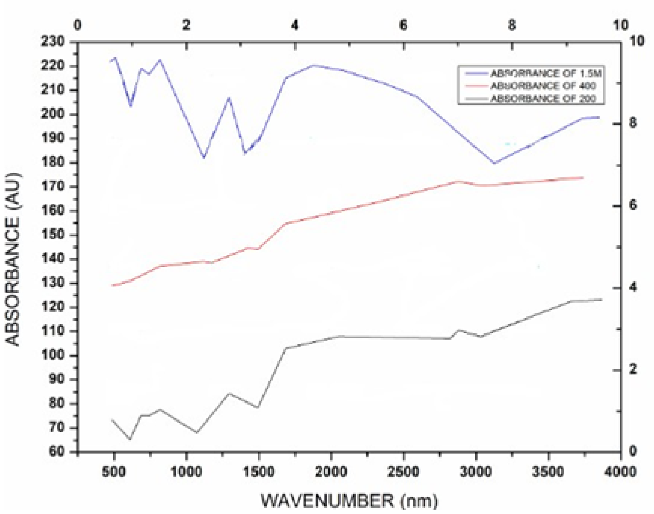


Fig. 1: Represents the variation of the Wavenumber to Absorbance of Pure PANI (1.5 M), PANI (200˚C), PANI (400˚C).

3. Results and Discussions

3.1 FTIR Characteristics:

FTIR is used for identification of organic molecular groups and compounds due to the range of functional groups, side chains and cross-linked involved, all of which have characteristic vibrational frequencies in the infra-red region. The frequency range is measured as wave numbers typically over the range 4000 – 600 cm^{-1}. This technique is based on the asymmetric molecular stretching and vibration of the chemical bonds.[10]

FTIR Analysis reveals the different functional groups that vary with temperatures. The characteristic bands of pure PANI exhibits alcohol compound of O-H Stretching at 3124.68 cm^{-1}, conjugated compound of C-O Stretching at 1685.79 cm^{-1}, halo compound of C- F Stretching at 1296.16 cm^{-1}, C-Br Stretching at 686.66 cm-1, C-Cl Stretching at 817.82 cm^{-1}. Similarly, the characteristic band of PANI (200˚C) reveals the presence of alcohol and O-H Stretching at 3032.10 cm^{-1}, C-O Stretching at 1683.86 cm^{-1}, C-F Stretching at 1294.24 cm-1, C-Br Stretching at 686.66 cm^{-1}, and C-Cl Stretching at 819.75 cm^{-1}.

The PANI (400˚C) confirms the presence of the characteristic band of alcohol compound of O- H Stretching at 3041.74 cm-1, conjugated ketone compound of C-O Stretching at 1681.93 cm^{-1}, halo compound of C-Br Stretching at 680.87 cm^{-1}, C-Cl Stretching at 810.10 cm^{-1}, C-F Stretching at 1068.56 cm^{-1}.

3.2 UV-VIS Spectrum Analysis

This Spectroscopy involves the absorption of the ultraviolet light by molecules causing the promotion of an electron from a ground state to an excited electronic state. This technique is useful in the determination of strength of the hydrogen bonding and identification of unknown compound, detection of functional group. The absorption bands of the PURE PANI are at 991 nm and at 242 nm which corresponds to the n – π* electronic transitions. PANI (200˚C) shows the absorption bands at 601 nm and 194 nm which corresponds to the n – π* electronic transitions. PANI (400˚C) shows the absorption bands at 1059 nm and 206 nm which corresponds to the π – π* transition and n – π* transition respectively. In this result, the band gap energy of pure PANI is found to be 1.25 e V and it is found to vary with the change in temperature.

Table 1: Reveals the variation of the characteristic bands of Pure PANI, PANI (200˚C), PANI (400˚C).

Groups	PURE PANI	PANI (200˚C)	PANI (400˚C)	Appearance
O-H Stretching	3124.68	3032.10	3041.74	Weak, Broad
C-O Stretching	1685.79	1683.86	1682.93	Strong
C-F Stretching	1296.16	1294.24	1068.56	Strong
C-Br Stretching	686.66	686.66	680.87	Strong

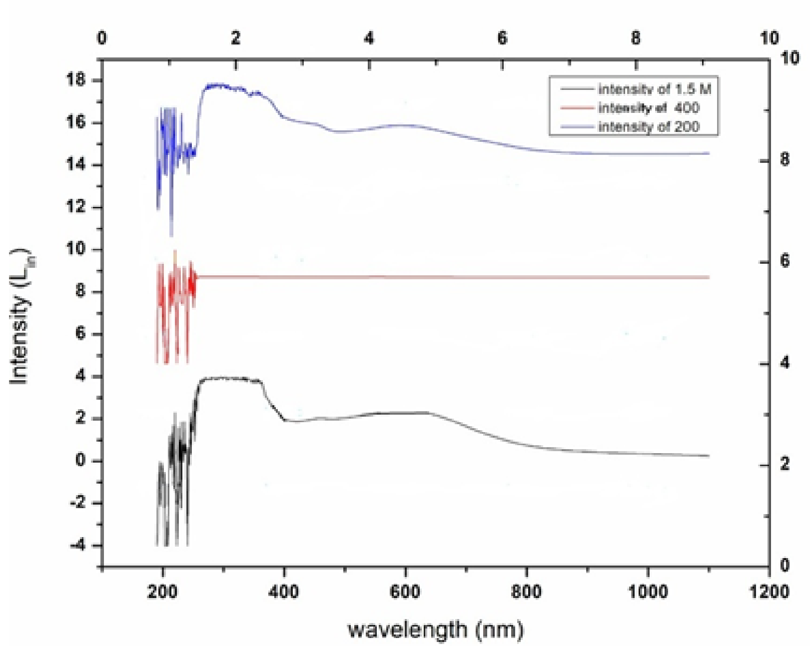
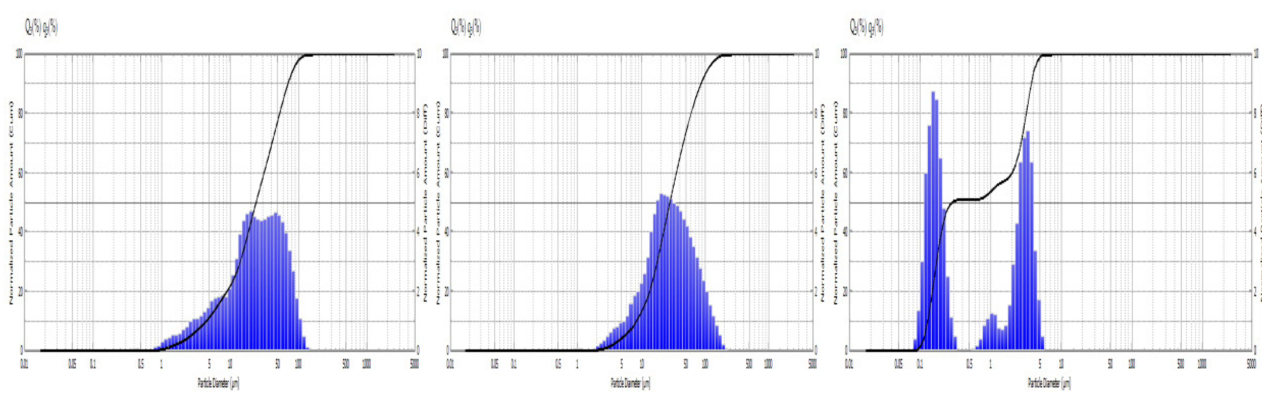


Fig. 2: Represents the variation of wavelength with Intensity of three samples Pure PANI, PANI (200˚C), PANI (400˚C).

Table 2: Represents the variation of the wavelength with respect to the absorption of the samples Pure PANI, PANI (200˚C), PANI (400˚C).

Sample Name	Wavelength In Nm		Absorption		Band Gap In Ev		Transition	
	Band 1	Band 2	Band 1	Band 2	Band 1	Band 2	Band 1	Band 2
PURE PANI	991	242	0.140	-0.802	1.25	5.12	n-π*	n-π*
PANI (200˚C)	601	194	2.367	-0.028	2.06	1.25	n-π*	n-π*
PANI (400˚C)	1059	206	0.061	-4.000	1.17	6.02	π – π*	n-π*



A B B

Fig.3: Represents particle size distribution of the prepared samples (A) Pure PANI, (B) PANI (200 ˚C), and (C) PANI (400˚C).

3.3 Particle size Analyzer

Particle size Analyzer provides information about the size distribution of particles. The particle size is designated as the average diameter in microns. It is based on the principle that angle of light scattering is inversely proportional to particle size. The normalized particle amount of Pure PANI at 25% was found to be 11.490, at 50% it was 23.769, at 75% it was 46.116. The results of PANI (200˚C) at 25% is 15.171, 50% was 27.372, 75% is 51.165. The results of PANI (400˚C) at 25% is 0.159, 50% is 0.286, 75% is 2.892.

Table 3: Reveals the particle diameter of samples Pure PANI, PANI (200 ˚C), PANI (400˚C).

Cum %	Particle Diameter (µm)		
	Pure PANI	PANI (200˚C)	PANI (400˚C)
25%	11.490	15.171	0.159
%	23.769	27.372	0.286
75%	46.116	51.165	2.892

3.4 Antibacterial activities:

Pure PANI can able to kill Staphylococcus aureus and Klebsiella pneumonia. PANI 200˚C can be able to kill all the bacteria like Bacillus, Cereus, Staphylococcus aureus, Escherichia coli, Klebsiella pneumonia at such amount noted in the Table 4. Then the PANI 400˚C can kill the bacteria like Bacillus cereus and Staphylococcus aureus and it does not able to kill the bacteria like Escherichia coli and Klebsiella pneumonia. The result represents the PANI 200˚C has a great

Table 4: Represents the antibacterial activity of Pure PANI, PANI (200˚C), and PANI (400˚C).

S. No	Micro organisms	Zone of inhibition in diameter (mm)					
		Pure PANI		PANI (200˚C)		PANI (400˚C)	
		50 µl	100 µl	50 µl	100 µl	50 µl	100 µl
1	Bacillus cereus	0	0	10	18	19	24
2	Staphylococc us aureus	12	15	15	19	8	10
3	Escherichia coli	0	0	17	20	0	0
4	Klebsiella pneumonia	10	8	18	20	0	0

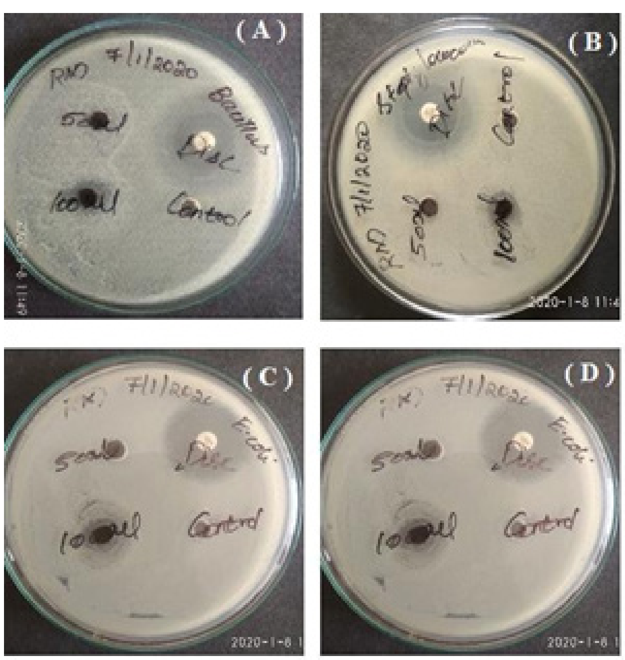


Fig. 4.1: Photographs of antimicrobial results of Pure PANI nanomaterial for gram positive (A) Bacillus cereus (B) Staphylococcus aureus (C) Escherichia coli (D) Klebsiella pneumonia.

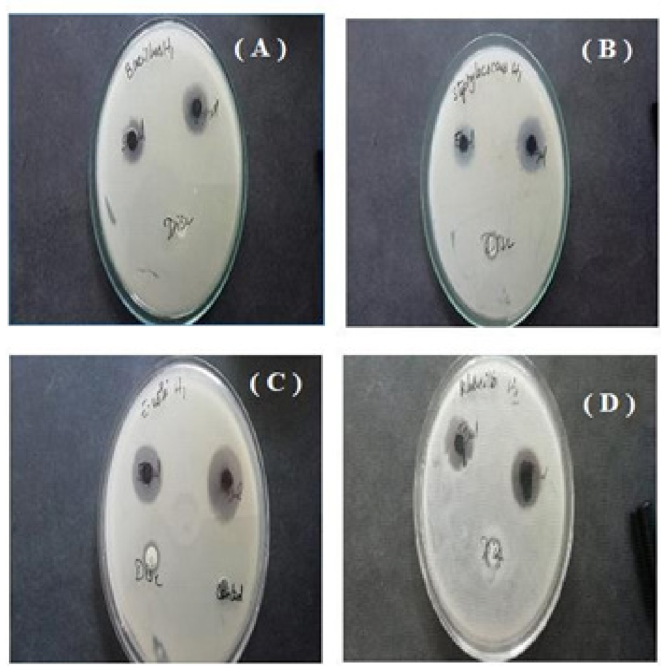


Fig.4.2 Photographs of antimicrobial results of PANI (200˚C) nanomaterial for gram positive (A) Bacillus cereus (B) Staphylococcus aureus (C) Escherichia coli (D) Klebsiella pneumonia

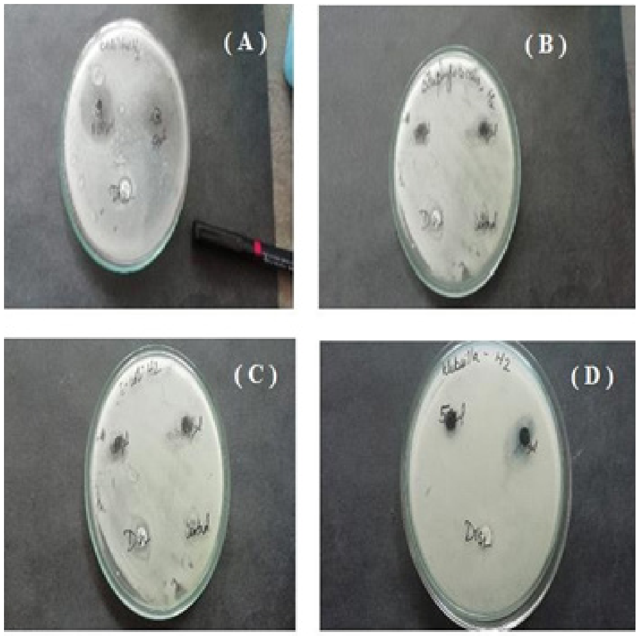


Fig.4.3 Photographs of antimicrobial results of PANI (400˚C) nanomaterial for gram positive (A) Bacillus cereus (B) Staphylococcus aureus (C) Escherichia coli (D) Klebsiella pneumonia

performance of antibacterial activity than the pure PANI and PANI 400˚C.

4. Conclusion

Polyaniline exhibits the change in the properties and their functional groups due to the annealing of temperature. The heat treated polyaniline at two different temperatures are found to exhibit the properties which slightly differ from that of the Pure PANI. FTIR exhibits the functional groups of the polyaniline samples and UV-Vis spectroscopy calculates the band gap energy. The results of particle size analysis show that the distribution of particle is greater for PANI (200˚C) than the Pure PANI and the value for PANI (400˚C) seems to be very low than that of the Pure PANI.

Reference

1. Nishara begum, N. Dhachanamoorthi, ME Raja Saravanan, P. Jayamurugan, D. Manoharan, V. Ponnusamy, Influence of annealing effects on Polyaniline for good microstructural modification, Optik, 124 (2013) 238–242.
2. S. Bhadra, D. Khastgir, NK Singha, JH Lee, Progress in preparation, processing, and applications of polyaniline, Prog Polym Sci., 34 (2009) 783–810.
3. Yu. Sapurina, J. Stejskal, Oxidation of Aniline with Strong and weak oxidants, Russian Journal of General Chemistry, 82 (2012) 256–275.
4. A.G. Mac Diarmind and A.J. Epstein, Polyanilines: a novel class of conducting polymers, Faraday Discuss Chem. Soc., 88 (1989) 317-332.
5. N. V. Bhat, N. V. Joshi, Investigation of the properties of polyacrylamide-polyaniline composite and its application as a battery electrode, Applied polymer, 50 (1993) 1423–1427
6. A.Rahy, D.J. Yang, Synthesis of highly conductive Polyaniline Nanofibers, Materials letter, 62 (2008) 4311–4314.
7. S. Bhadra, D. Khastgir, Extrinsic and Intrinsic structural change during heat treatment of polyaniline, Polymer Degradation and Stability, 93(6) (2008) 1094–1099
8. J. G. Masters, Y. Sun, A.G Mac Diarmid, A.J. Epstein, Polyaniline: allowed oxidation states, Synthetic metals, 41 (1991) 715 – 718.
9. A.J. Epstein, H. S. Woo, D.B. Tanner, W. S. Huang, A.G. Mac Diarmid, Infrared and Raman Study of Polyaniline part I. Hydrogen bonding and electronic mobility in emeraldine salts, Phys. Rev. Lett., 59 (1987) 1464–67.
10. M. Reka Devi, A. Saranya, J. Pandiarajan, J. Dharmaraja, N. Prithivikumaran, N. Jeyakumaran, Synthesis, Electro Chemical and Optical Performance of Organic Acids Doped Polyaniline (PANI), Journal of Applied Science and Engineering Methodologies, 2(3) (2016) 317–321.