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Synthesis and Characterization of Polyaniline Nanomaterials with different Molar Ratio of Monomer

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Abstract

Formation of polymer nanomaterials are achieved by the process of polymerization and there was an availability of different methods such as chemical oxidative polymerization, electro chemical polymerization, In-situ oxidative polymerization and emulsion polymerization etc., Many monomers combine to form polymers under certain conditions by chemical reactions between the monomers. The chemical oxidative polymerization was most commonly used method to synthesize PANI and the synthesis process involved various molar ratio of aniline (0.1M, 0.2M, 0.3M) in which APS was used as an oxidant with dopant of HCl. This study revealed that the properties changed based on their initial conditions. The prepared aromatic polyaniline was characterized by FT-IR, UV-VIS, Particle size analyzer techniques and anti-bacterial activity of the sample was analyzed. FT-IR spectroscopy gives deep view of many functional groups that were present in a system by measuring vibrational frequencies of chemical bonds involved. UV-VIS was a good tool to identify, characterize and to study the optical properties of nanomaterials. In particle size analyzer, the size of a particle was measured using the instrument laser diffraction particle size analyzer (SALD-2300). The synthesized polyaniline had the tendency to resist the growth of both gram positive and gram negative bacteria. These organic conducting polymers were sometimes called "smart polymers" and have varies application in medical, OLED, solar cell, batteries and sensor etc.,

Keywords: Aniline, chemical oxidative polymerization, polyaniline.

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1. Introduction

The developing interest in Nano sized polymers is due to enlarged area of their practical applications. With the discovery of polyacetylene in 1958, the golden era of conducting polymers had started.[1] The functional groups of conducting polymers have pseudo capacitance characteristics and thus show conductivity as material itself.[2] Among many conductive polymers, polyaniline had attracted an enormous application due to its environmental stability, ease of synthesis and doping/ de-doping chemistry.[3] Polyaniline can undergo reversible redox reaction which is used for fuel cell applications.[4] The conducting nature of PANI depends on its dopant type, oxidation states and degree of protonation. It has high specific capacitance. When aniline is polymerized, the resultant polyaniline can exist in any one of three idealized oxidation states: 1) emeraldine base (EB) 2) leuco emeraldine (LEB) 3) per nigraniline (PEB).[5] The charge carriers in polyaniline are polarons and bi polarons sustained by counter ions (which maintain electric neutrality) assimilated into polymer during synthesis process. The conductivity and physical properties of PANI hangs on selection of counter ions.[6] Usually pure PANI is colourless and oily, when exposed to light and heat the colour turns to brown. It is an acid type. In old ages, polyaniline was entitled as "aniline black". Such polyaniline is used in various applications such as anti-corrosive coatings, LED, electromagnetic shielding, diodes, sensors, anti-static coating and so on.[7-9]

In our pioneering work, we describe the synthesis and characterization of polyaniline which is prepared by chemical oxidative polymerization method with the presence of dopant and oxidant. This method does not need any special instruments and it is a fast process.

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2. EXPERIMENTAL PROCEDURE

Polyaniline commonly known as PANI is prepared by chemical oxidation polymerisation method. In this method, aniline is polymerised with the help of chemicals. In this preparation, Hydrochloric acid plays the role of dopant and Ammonium peroxy disulphate as an oxidant. The organic aniline, which is the main material, is taken in different molarities such as 0.9130 ml (0.1M), 1.8260ml (0.2M) and 2.7391ml (0.3M). The monomer aniline was dissolved in 100ml of distilled water and this combination is stirred in magnetic stirrer for five minutes. After 5 minutes, 3.0898ml of Hydrochloric acid is added drop by drop and it is allowed to stir for half an hour at constant stirring of 600 rpm. Then, 2.8525g of Ammonium peroxy disulphate salt is mixed with 25ml of distilled water. This mixture is added dropwise to the above solution. During the addition of Ammonium peroxy disulphate mixture to the solution, the colour change is observed. The solution changes to dark green which represents the polymerisation. This solution is allowed to stir for 24 hours at 500 rpm.

After 24 hours, blackish green precipitate of polyaniline was obtained. Then the precipitate was filtered using Whatmann filter paper. To wash out the impurities and excess acid, it is washed with 20ml of Acetone and then with 25 ml of Ammonia. At last, the wet precipitate is obtained. It is dried for 3 days under vacuum at 60°C. The dried precipitate is finely grinded using agate mortar and is collected in a sample box. The same procedure is repeated for different molarities of Aniline. The yield of polyaniline for, 0.1M of aniline is 1.766g, 0.2M of aniline is 1.171g and for 0.3M of aniline is 1.315g.

3. RESULTS AND DISCUSSIONS

3.1 FTIR Spectral Analysis

FTIR is the most famous method to examine changes in the composition due to oxidative ageing. Generally, the aim of Fourier Transform Infrared Spectroscopy (FT-IR) is to give information about light absorption (infrared radiation) of a sample at a determined wave number from 4000 cm^{-1} to 400 cm^{-1}.

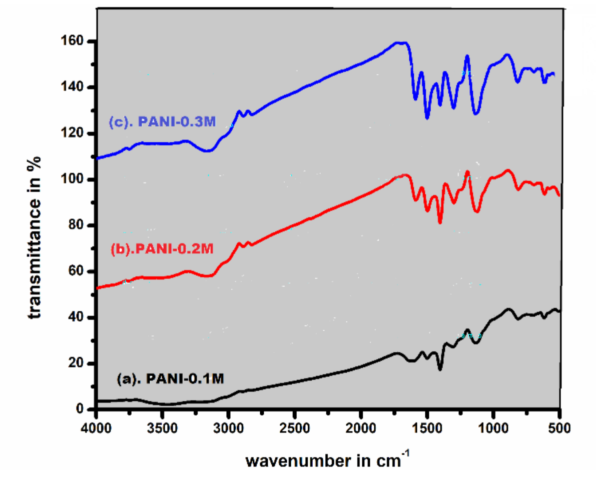

Fig. 1: FTIR Spectra of PANI (0.1M, 0.2M, 0.3M)

In this study, FTIR spectra (Fig. 1) for polyaniline prepared by various moles of aniline (0.1M, 0.2M, and 0.3M) were recorded. The functional groups can be written by comparing the results of our samples with materials in FTIR library. Comparing the results of these three samples, the maximum transmittance peak is ranging from 3200 cm^{-1} to 2700cm^{-1}. So, it attributes to O-H stretching vibrations and has an alcohol compound of weak bonds. The second maximum peaks for three samples were 1625.99cm^{-1}, 1587.42cm^{-1}, 1589.34cm^{-1}. These peaks assigned to N-H bending of amine groups with medium bonds. The next peak appeared at 1404.18cm^{-1} having carboxylic acid compound of medium O-H bending vibrations. The presence of aromatic amine compound corresponds to C-N stretching strong bonds are shown by the spectrum peaks lies between 1303.88cm^{-1}-1298.09cm^{-1}. This proves the presence of amine groups with medium bonds. The transmittance peak seen at 813.96cm^{-1} could be attributed to strong C-Cl stretching of halo compounds. The intensity decreases with the decrease of transmittance peak. Hence FTIR spectroscopy confirms the presence of functional groups and it may also use to characterize the surface nature of nanoparticles. Table 1 gives the values of stretching vibrations for prepared PANI.

3.2 UV-VIS Absorption Spectral Analysis

UV-VIS was a good tool to identify, characterize and to study the optical properties of nanomaterials. It gives the absorption value by the measuring the intensity of light which passes before and after through the sample. It is used to determine the strength of hydrogen bonding.[10] The π* and n* orbital was known to unoccupied or antibonding orbitals. Fig. 2 gives the results of optical spectrum of PANI prepared using 0.1M, 0.2 and 0.3M of aniline.

The wavelength for 0.1M PANI lies between 1027.00 nm and 205.00 nm which corresponds to π-π* and n-π* transition. For 0.2M, the maximum value of wavelength is

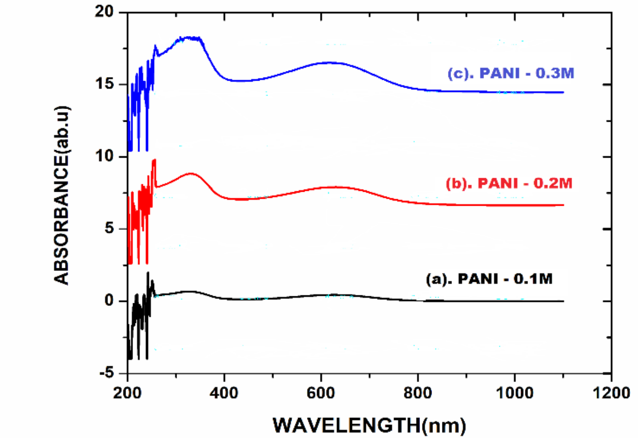

Fig. 2: UV-VIS Spectra of PANI (0.1M, 0.2M, 0.3M)

Table 1 : Stretching vibrations for 0.1M ,0.2M ,0.3 M of PANI.

VIBRATIONS	COMPOUND NAME	WAVENUMBERS (cm-1)		
		0.1M	0.2M	0.3M
O-H Stretching vibrations	Alcohol	3197.98	3169.04	3167.12
N-H Bending vibrations	Amine	1625.99	1587.42	1589.34
O-H Bending vibrations	Carboxylic acid	1404.18	1404.18	1404.18
C-N Stretching vibrations	Aromatic amine	1303.07	1298.09	1300.02
C-Cl Stretching vibrations	Halo compounds	813.96	812.03	817.82

Table 2: Peaks, electron transition and band gaps of PANI (0.1M, 0.2M, 0.3 M)

SAMPLE NAME	WAVELENGTH (nm)	ABSORPTION (%)	TRANSITION	BAND GAP (eV)
PANI (0.1M)	205.00	-4.000	n-π^*	6.0528
	1027.0	0.007	π-π^*	1.2082
PANI(0.2M)	256.00	3.187	n-π^*	4.8470
	1092.0	0.041	π-π^*	1.1363
PANI (0.3M)	219.00	1.288	n-π^*	5.6659
	1053.0	0.041	π-π^*	1.1784

1092.00 nm and attributes to π-π^* transition. The minimum value of wavelength is 256.00 nm and has n-π^* transition. For 0.3M, the maximum wavelength is 1053.00 nm with π-π^* transition and minimum wavelength is 219.00 nm with n-π^* transition.

Generally, the absorption values of the samples were compared with the wavelength it is shown that for higher wavelength the absorption rate was minimum and vice versa. On comparing the results of three samples the maximum wavelength is for 0.2M (1092.00 nm) and the minimum wavelength is for 0.1M (205.00 nm). From those maximum and minimum wavelengths, we can calculate the band gap energies of the samples using the formula Eg = (h×c)/wavelength(max/min) (joule) where, h is Planck's constant (6.626×10^{-34} m^2kg/s) and c is speed of light (3×10^8 ms^{-1}). The band gap energies of synthesized PANI were compared in the Table 2.

3.3 Particle Size Analysis

A particle size was measured using the instrument laser diffraction particle size analyzer (SALD-2300). The synthesized PANI samples with different moles of aniline

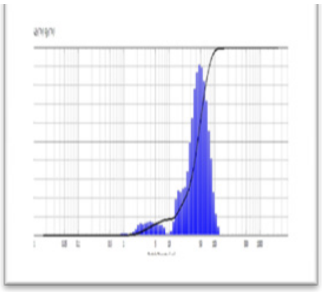

Fig. 3.1: PSA of 0.1M

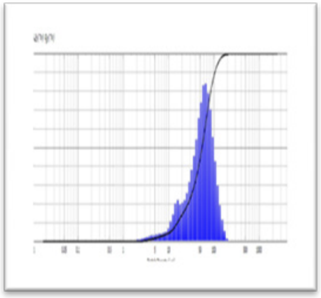

Fig. 3.1: PSA of 0.2M

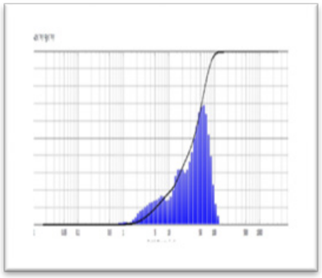

Fig. 3.1: PSA of 0.3M

were given under the test to analyze the particle size distribution. The graph was drawn between particle diameter (µm) in x-axis and normalized particle amount (cum%) in y-axis for the three samples were in figures (3.1, 3.2, 3.3). As the cum% decreases the diameter also decreases. Table 3 shows the variation of diameter with the cum% for three different samples.

In PANI 0.1M, the particle diameter for normalized particle amount(cum) 25% is 27.074µm, then for 50% is 41.995µm and for 75% is 59.093µm. Finally, the average value for 0.1M is 42.720µm. In PANI 0.2M, the diameter for cum 25% is 31.533µm, then for 50% is 54.022µm and for 75% is 78.302µm. the mean value is 54.619µm. In PANI 0.3M, the diameter for cum 25% is 14.465µm, for 50% is 57.201µm and for 75% is 35.570µm. The mean value is 35.570µm.

Table. 3 CUM% and PANI Diameter for 0.1M, 0.2M, 0.3M

CUM%	PANI DIAMETER (µm)		
	0.1 M	0.2 M	0.3 M
25	27.074	31.533	14.456
50	41.995	54.022	35.046
75	59.093	78.302	57.201
AVERAGE	27.074	54.619	35.570

3.4 Antibacterial Activities

The antibacterial activity of polyaniline (0.1M, 0.2M) against Staphylococcus aureus (gram positive), bacillus cereus (gram positive), Escherichia Coli (gram negative) and Klebsiella Pneumoniae (gram negative) bacteria were examined and growth inhibition is calculated in millimetre.[11] The prepared polyaniline samples were trusted to play a role of antibacterial agent as well as multi-functioning material for developing the health of homo sapiens and other living things.

The given sample was tested for antimicrobial activity by well diffusion method. Liquid Mueller Hinton agar media and the Petri plates were sterilized by autoclaving at 121o C for about 30 minutes at 15 lbs pressure. Under aseptic conditions in the laminar airflow chamber, about 20ml of the agar medium was dispensed into each Petri plate to yield a uniform depth of 4mm. After solidification of the media, 18 hrs culture of Gram positive microorganisms such as Bacillus cereus (MTCC 430), Staphylococcus aureus (MTCC 3160), Gram negative microorganisms such as E. coli (MTCC 1698) and Klebsiella pneumoniae (MTCC10309) obtained from IMTECH, Chandigarh were swabbed on the surface of the agar plates. Well was prepared by using cork borer followed with loading of 50 µl and 100 µl of each sample to the distinct well with sterile distilled water as negative control and ampicillin (30mcg/disc) as positive control. The sample loaded plates were then incubated at 37°c for 24 hours to observe the zone of inhibition.

Fig. 3.4.1: PANI (0.1) *E. coli*

Fig. 3.4.2: PANI (0.2) *E. coli*

Fig 3.4.3: PANI (0.1M) Klebsiella Pneumoniae

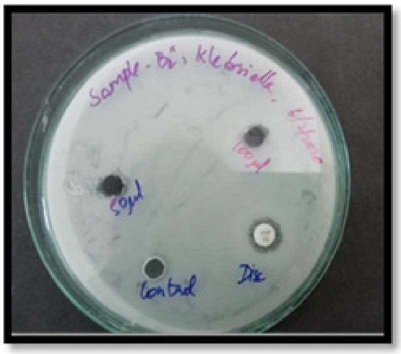

Fig. 3.4.4: PANI (0.2M) Klebsiella Pneumonia

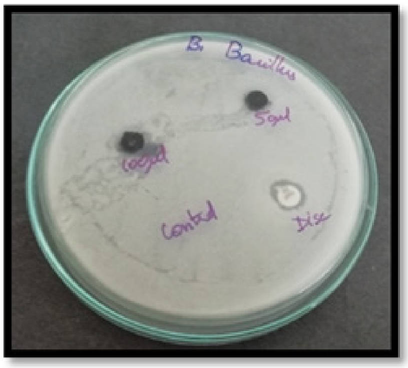

Fig. 3.4.5: PANI (0.1M) Bacillus cereus

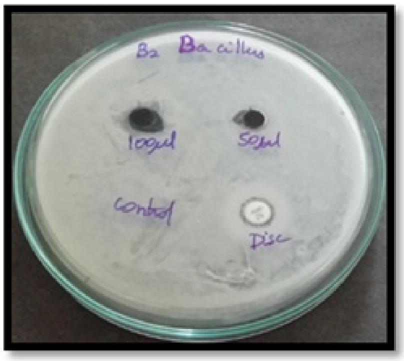

Fig. 3.4.1: PANI (0.1) E. coli

Fig. 3.4.7: PANI (0.1M) Staphylococcus aureus

Fig. 3.4.1: PANI (0.1) E. coli

Table 4: Antibacterial results of PANI – 0.1M and 0.2M

Sample Name	Zone of inhibition in diameter (mm)							
	Gram Positive				Gram Negative			
	Staphylococcus aureus		Bacillus cereus		Escherichia coli		Klebsiella pneumoniae	
	50 µl	100 µl	50 µl	100 µl	50 µl	100 µl	50 µl	100 µl
PANI 0.1M	10	15	0	0	0	0	10	18
PANI 0.2M	0	0	0	0	0	0	0	0

4. CONCLUSION

The aromatic polyaniline was successfully synthesized by chemical oxidative polymerization method in which Ammonium peroxy disulphate was used as an oxidant with dopant as Hydrochloric acid and the samples were named as PANI (0.1M), PANI (0.2M) and PANI (0.3M). The prepared polyaniline was triumphantly characterized by Fourier transform infrared spectroscopy (FTIR), UV-VIS, Particle size analyzer techniques and its antibacterial activities was also analyzed. The FTIR spectroscopy shows the presence of amine group by measuring vibrational frequencies of chemical bonds involved. UV-VIS gives the band gap energies of the prepared samples and those Values were compared. Particle size analyzer admirably gives the diameter of PANI (0.1M, 0.2 and 0.3M) and it was found to be 27.074 µm, 54.619µm, and 35.570µm respectively. The prepared PANI- 0.1M had resisted the growth of gram positive and gram negative bacteria to some extent. The 0.2M PANI does not shown any antibacterial activity. This study successfully gives the results for changing the molarities of aniline in the synthesis process of its polymer.

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