SYNTHESIS, CHARACTERIZATION AND STUDY OF NOVEL POLYANILINE NANOPARTICLES AND NANOFIBER

[1]Jumaa W. Salem, **[2]Abdul Adheem Zaily Hameed**, **[3] Tariq Abdul Jaleel Mandeel**

[1, 3] Al-Huda University College, Department of Fuel and Energy Techniques Engineering , Anbar Ramadi, Iraq. [Email: jumaa.w@uoalhuda.edu.iq

[3]University of Anbar, College of Computer Science & Information Technology, Computer Science Department, Anbar, Ramadi, Iraq.

Corresponding author :[E-mail: ab72d74@uoanbar.edu.iq]

Abstract

In the present paper, novel polyaniline PANI nanoparticles and Nanofiber have been successfully synthesized. In situ polymerization method (chemical method) used to preparation polyaniline conductive polymers. Ultrasonic welder of 20 kHz used to reach very small spherical nanoparticle size. X-ray diffraction (XRD), Transmission electron microscope (TEM),Scanning electron microscope(SEM), H-NMR Spectrum photometer and Fourier transform infrared (FT-IR) spectroscopy analysis used to study the structures, morphology and particle size of novel PANI nanoparticles. According to XRD, the crystal size of the nanoparticles with the range of 2.5-3.7A° and the TEM images illustrated that the particles have spherical shape with the diameters between 6.61-17.14 nm .Polymers blends were prepared (PANI+ Poly a-methylstyrene) and (PANI+ Polymethylstyrene), electrical conductivity for blend are 1x 10 $^{-4}$ Scm$^-$ at 25C^0,and composite have conductivity the same of semiconductors.

Index Terms —*Nano polyaniline, composite, nanoparticles, polymerization, Polymers blends*

1. Introduction

Polyaniline has been focused in wide studies due to its several unique properties. Easy of synthesis, good environmental stability, high conductivity and unique optical properties make it very attractive in scientific and technical interest for many practical applications, such as corrosion inhibitors, microelectronical devices and PH or gas sensors [1,2,3]. Many methods have been developed to make nanostructures of polyaniline with diameters smaller than 100nm by introducing structural directing agents during the chemical polymerization reaction [4]. In spite of these excellent properties, insolubility ,brittleness and poor mechanical properties of pure PANI limit their processability in commercial applications. Blending with water soluble polymers such as PVA, poly (vinyl pyrrolidone) etc. improved these properties and make PANI to be more processable in forming composite [5,6]. Polyvinyl alcohol (PVA) used in a lot of medical applications, because several advantages such as high biocompatibility, biodegradability, hydrophilicity, and ability to form fiber [7,8]. Some studies looked at the relations between crystallinity, morphologies, and particle size as a function of time during ultrasonic irradiation. The data showed that the particle size increased as the reaction time increased. All of the data showed that as the ultrasonic irradiation reaction time increased, the particle size of polyaniline nanoparticles increased [9].

2. Experimental Details:

Chemicals: Aniline (Merck) used after double distillation. Methylacrylic and a-methylstyrene, petroleum ether were procured from Fluca Co, and used after purifications by standard method(double washing with 5% NaOH and vacuum distillation).$K_2S_2O_8$, HCl, H_2SO_4, KIO_3, NaOH and DMF from Sigma- Aldrich Co. All solvents used after purification.

Apparatus: FT-IR spectra were recorded on Nicoletir 100FTIR – spectrometer from 4000 to 400 cm for samples in KBr disc form. Transmission Electron Microscope TEM-FEI ORPORATE HEADUARTERS- Quanta 200FEG. X-Ray Diffraction Rigaku company micro max 007 HFDW. Ultrasonic Equipment –Hielscher/ Germany UP400S.

Synthesis of polyaniline PNA nanoparticle

A repeated distillation process was used to purify the aniline. The aniline manufacturing process was carried out through the chemical oxidation of aniline. Aniline monomers dissolved in an aqueous solution with a strong acid solution of 1M HCl at 0°C. (1M) magnetic stirrer and 1 g of KIO3 were added to 100 mL of used H 2 S o 4 to obtain a uniform solution. Then, 1 ml of distilled aniline monomers was placed in a stirred aqueous solution and the reaction was carried out at 25°C for 5 hours. Consequently, the resulting dark green polymer was filtered through filter paper to remove oligomers and impurities, washed several times with doubly ionized water and dried at 60°C in an oven for 24 h. To obtain the polyaniline nanoparticles powder dissolved in ionization water and 20 minutes of magnetic stirring, then ultrasonic welding at 20 kHz at 0°C for 20 minutes is used.

Synthesis of polyaniline PNA Nanofiber

By combining [2ml] of aniline with [200ml] of strong acid [1M] and cooling the mixture at [0–5°C], PANI was created. Using 200 ml of H2SO4 [1M] and stirring for 10 minutes, 2 g of KIO3 (0.01 M) was dissolved to create the oxidant agent. For five hours, the oxidant agent and acidic aniline solution were slowly combined while being constantly stirred. Gradually, the color of the combination changed to yellow, brown, pink, purple, blue, and blackish green. The resulting green-blackish precipitate was filtered and rinsed with distilled water several times until the color disappeared and the filtrate became colorless. The filtrate was then dried for an entire day to remove moisture 50 to 60 degrees Celsius in the vacuum oven. 90% of conversions actually occur. 90% of conversions are made.

Characterizations PANI Particals:

The structural properties of the prepared PNA nanoparticles were investigated by high-resolution X-ray diffraction (HR-XRD) using an X'Pert Pro MRD diffractometer system (PANalytical Corporation) equipped with a wavelength of Cu-Kα radiation (λ = 0.15418 nm.) operating at 40k. volts and 20mA. Transmission electro microscopy (TEM) images were taken using a Philips CM-12 transmission electro microscope .The chemical structures of PANI nanoparticles are characterized by infrared spectroscopy (FT-IR) (Bruker Optics Ft Tensor, Germany) using KBr discs.

Polymerization of a-methylstyrene:

Polymerization of a- methylstyrene was occurred at 70 °C for 5 hours in three necked round bottom with 80 ml ethanol, under stirring device was charged 5 ml of monomer, potassium persulfat 0.45gm as initiator added to polymerization solution, The product was washed with petroleum ether 60% and dried at $40C^0$ in vacuum oven for 72hrs. The conversion % of polymer **(Pa-MSt)** was 25%.

Polymerization of methyl acrylate (MA) carried out the same procedure of a-methylstyrene polymerization.

Synthesis of polymers blends:

Blend of PANI + PMA: plymethylacrylat (PMA) 1.5gm dissolved in 80ml methanol in 250ml beaker. To 0.35gm of aniline (monomer) and 3.3ml of 1M HCl soltion added, 15ml of 0.15ml
 Initiator potassium persulfat was added drop by drop while the content was being stirred.. The reaction was carried out at $50C^0$ for 7hrs the blend was precipitated in distilled water. Filtered and dried in a vacuum till moisture was removed .In 3*10 cm glass sheet film was casting by dissolving the prepared blend in DMF.
Distilled potassium persulfate initiator was added to the stirred reaction mixture. The reaction was carried out at 50°C for 7 h, and the mixture was precipitated from distilled water. Filter and vacuum dry until moisture is removed. At 3 * 10 cm, a film of glass plates is poured by dissolving the prepared mixture in DMF.

Electrical conductivity measurement:

Electrical conductivity were measured for blends specimens (PANI + PMA) and (PANI + Pa-MSt) and other method in different concentration of conductive polymer PNAI composite on the insulators polymers (PMA, Pa-MSt) via an electrical laboratory cell had been designed for this purpose. The conductivity was calculated by Ohm' s law ,where : σ = (I*L / A*V), where ... A = area of the cross-section cm^2, I = current amps, L = length samples in cm, and resistance also represents the reversal of electrical conductivity ", where (σ) = (I / V) , ("$\Omega^{-}cm^{-1}$ = S cm^{-1}") .

3. Results and Discussion

Characterizations of PANI Nanofiber:

The structural properties of the prepared PNA Nanofiber were examined using the same previous of instruments and NMR instrument.
The PANI aggregation displays many types of nanofibers with lengths ranging from "The range of sizes was (562.0 ± 3.3 to 85.0 ± 3.0) nm (Av. 352.0 ± 3.4) , with a mean diameter of about 40.0 ± 2.3 nm. These spherical nanoparticles self-assemble into fibrous forms with sizes ranging from ((8.0 ± 1.2 to 49.0 ± 2.8) nm, with an average size of about 16.5 ± 1.8 nm ". as seen in figure (1).
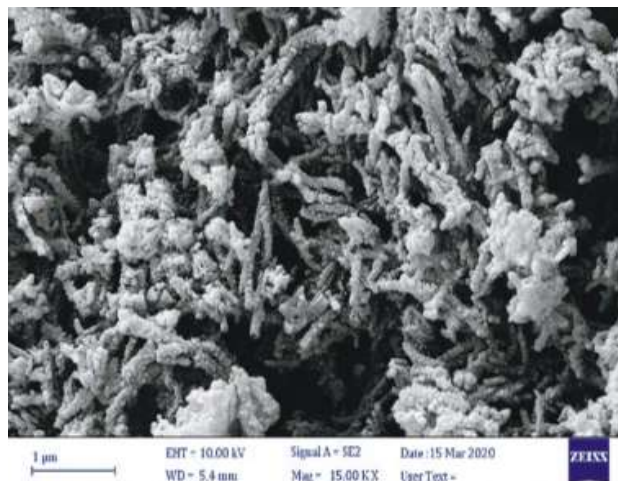
Fig. (1): FE-SEM for the PANI Nanofiber

H-NMR Spectrum of PANi

Synthesis of PANI compounds was obtained from DMSO technology performed at 500 MHz. Nuclear Magnetic Resonance (NMR) probe in BB 05 mm and the standard peak used was TMS at a room temperature of 24 °C. The outcomes were analyzed using chemotherapeutic software.

At (2.49 ppm and 3.50 ppm) two strong peaks were noted due to the water absorption by DMSO. peaks (6.96, 7.07, and 7.19) appear attributable to the nitrogen atom and hydrogen atom. at (9.32, 9.31, and 8.29) ppm appear to be secondary amine (-NH-) as well as those of the aromatic ring of (7.21 2H, 6.77 2 H, 7.37 2 H, 7.32 2 H) for (Hb, Hc and Hd) in parallel. They are 7.17 2H, 7.21, 5.78 and 7.13, 5.81, and 5.82 ppm for (Hf, Hg, and H1). The NMR for NIBP is shown in Figure (2).
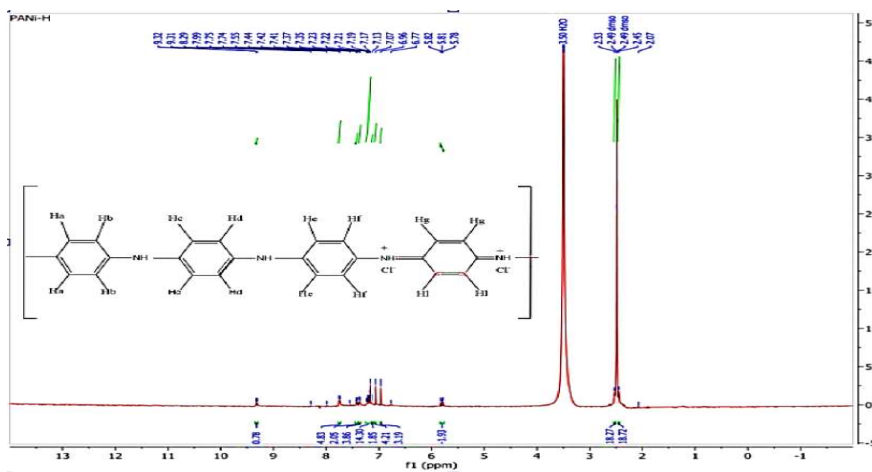
Fig. (2):   1H-NMR spectrum for PANI .

FT-IR Spectrum for PANI

Figure 3 shows the spectrum of the FTIR. Compound PANI (3359 to 3223) cm−1 board peak indicates the stretching vibrations (NH) of minor amine. (1556 and 1522) cm−1 for the double bond of carbon to the quinonoid cycle. 1482.43 cm-1 double bond for stretching vibrations of the benzenoid cycle at (1244 and 1302) cm-1 for (C-N) stretching vibrations of the secondary aromatic cycle. These results coincided with Results from researchers Ajeel and Kareem .
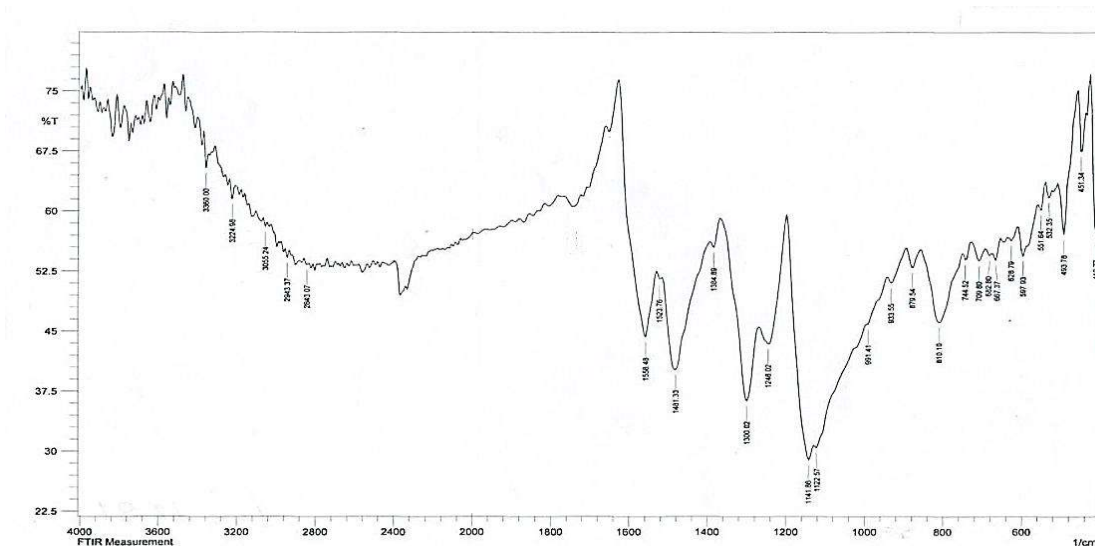
Fig. (3): FT-IR spectra of a PANI

### Structural Analysis: X-ray diffraction

Figure1 shows the evolution of X-ray diffraction patterns of the prepared PANI nanoparticle. It is clear that the XRD pattern of PANI suggests that it exhibits a semi crystalline behavior . X-ray diffraction of PANI nanoparticles recorded at room temperature shows two diffraction peaks at respectively 2θ = 21.258° and 2θ = 24.496° which are the characteristic peaks of PANI (Mexiang Wan et al 1994). Table1 shows XRD parameters of Polyaniline Nanoparticles. Bragg's law and Scherrer's Eq. used to calculate the inter-planar distance and the crystallite size of PANI nanoparticles as shown

$$D = \frac{0.89\lambda}{\beta \cos\theta}$$

Where D is the mean crystalline size, λ wavelength of Cu K (1.54A°), θ is the Bragg angle in degree and β is the full width at half maximum intensity (FWHM) [8, 9, 10]. One can see from the X-ray pattern that PANI is not very crystalline and whole diffraction pattern is very noisy so that, the interplanar spacing d [A°] is only approximate.

**Table.1 Physical parameters of PANI Nanoparticles XRD**

2θ	FWHM	d-spacing (A°)	Crystallite size
21.258°	0.3936	4.17956 A°	3.7364 A°
24.496°	0.5904	3.63401 A°	2.5511 A°
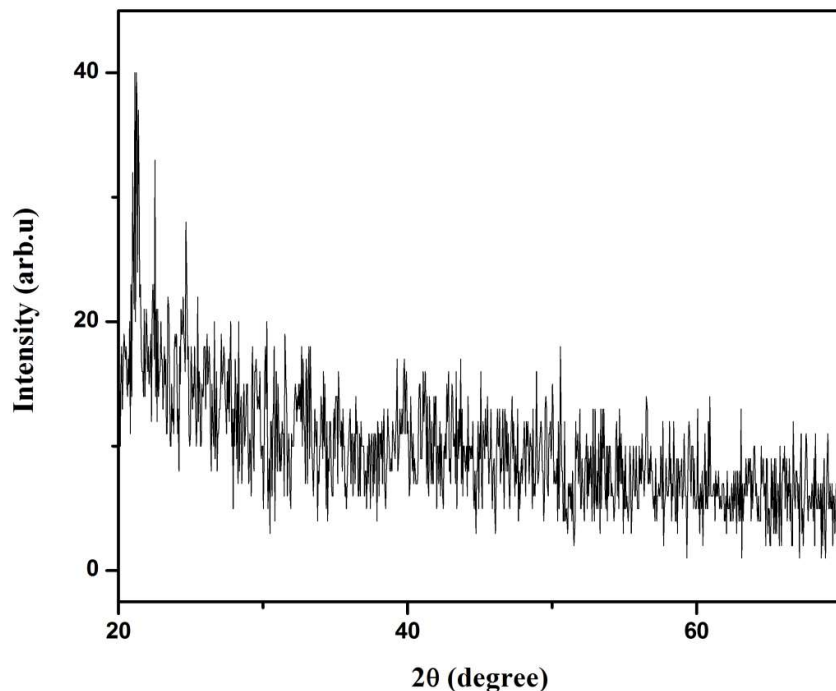
Fig .4 XRD Pattern of PANI nanoparticles

Transmission electron microscopy (TEM)

The morphology of the PANI nanoparticle has been characterized in further detail using TEM. The following sample preparation procedure was used to perform this measurement. One drop of the aforementioned dispersion was applied to a carbon-coated (Cu grid) after the PANI nanoparticle was dipped in ethanol and sonicated for 10 min. The grid was utilized for TEM measurement after allowing the solvent to evaporate. The TEM images of PANI nanoparticles are shown in Fig.5. As showing in Fig.5 nanoparticles look spherical with diameters between 6.61nm and 17.14nm which is very large than the crystallite size that measured by XRD. These results indicated that there are some crystallites in PANI. [9].
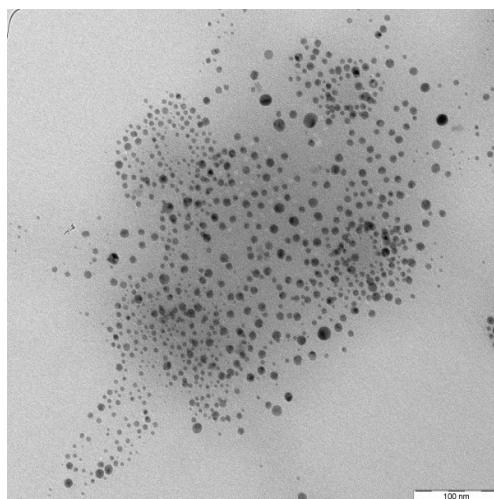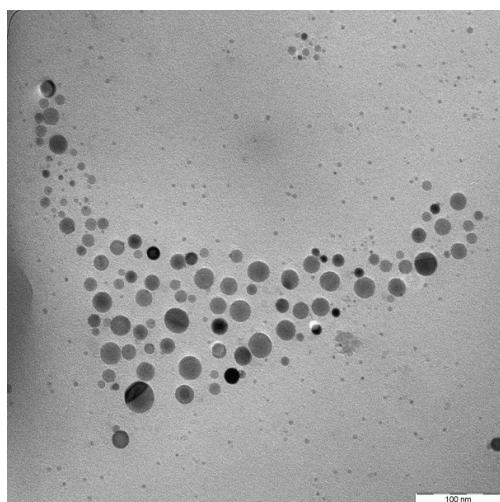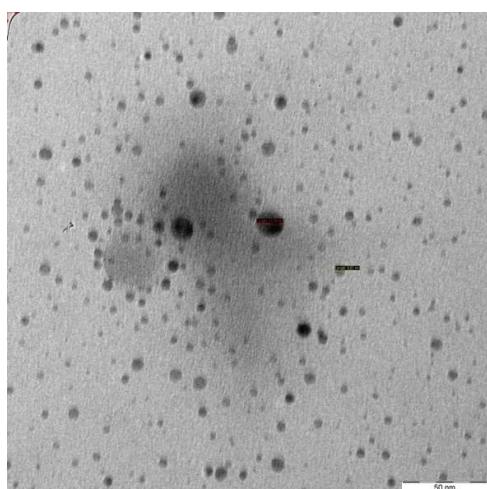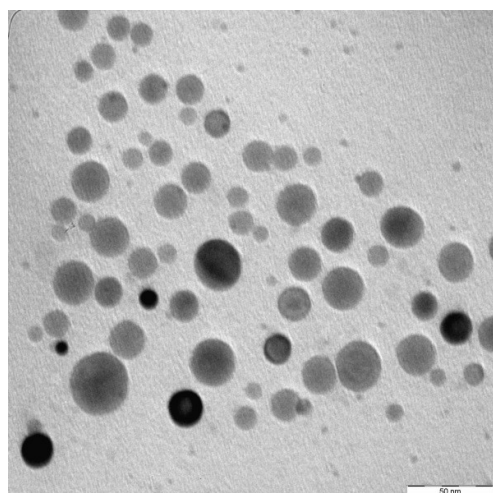
**Fig. 5 TEM images of PANI nanoparticles**

Electrical conductivity:

Conductivity of blend film was calculated from the fallowing equation: [10, 11]

$$\sigma = \frac{\ln 2}{(\pi R t)}$$

R is the resistance of the sample and t is the thickness in cm. 1x 10 $^{-4}$ Scm^{-} at 25C^0 the conductivity of film blend which was effected by the thickness of the film.

Electrical conductivity of composites (PANI + PMA) and (PANI + Pa-MSt) carried out via an electrical laboratory cell had been designed, **Scheme. 1** which was effected by the concentration of PANI **Table.2**.And conductivity of the composites increase as concentration of PANI increase. However, the composites have as semiconductors properties at ($10^3 - 10^{-12}$ SCm^{-1}), **Figure.6** but an Insulators have low conductivity ($10^{-12} - 10^{-22}$ SCm^{-1}).
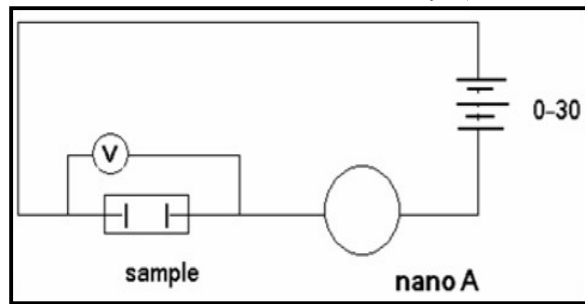
Scheme. 1. electrical circuit for measurement of the conductivity.

Table. 2. Values of Electrical Conductivity of Composites in different concentration

Blends	n.	Conc.%	I nA	V (volt)	Cond. (S)
PANI + P(a-MSt)	1	0.02	0.0000002	29.9	6.68896E-09
	2	0.002	0.0000001	29.9	3.34448E-09
	3	0.0057	0.00000003	29.9	1.00334E-09
PANI + PMA	1	0.08	0.0000001	29.9	3.34448E-09
	2	0.011	0.0000001	29.9	3.34448E-09
	3	0.022	0.0000002	29.9	6.68896E-09
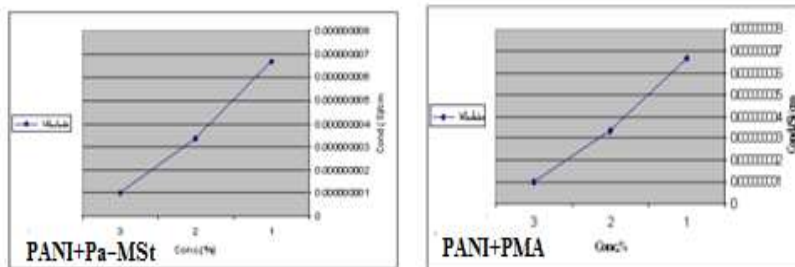
Fig. 6. Relationship between conductivity and concentration of PANI in composites.

4.Conclusion

Structural properties of PANI nanopartical were Successfully prepared by chemical polymerization of aniline was carried out by XRD showed the semicrystalline array of the nanoparticles and the TEM images illustrated the spherical shapes of this particles with diameters between 6.61nm and 17.14nm. XRD and FT-IR peaks were identical to the characteristic peaks of polyaniline and showed some crystalline structure. The electrical conductivity of blend and composites polymers were a good result due to prepared of the semiconductors materials from insulators. That can be used as small chipset in electronic circuits.

5.References

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