Effect of Surfactant on Morphology and Conductivity of Polyaniline Nanoparticles Prepared in Water/Tetrahydrofuran Solution

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Polyaniline nanoparticles were synthesized in a water/tetrahydrofuran solution by using KIO_3 as an oxidant in the presence of various surfactants such as hydroxypropylcellulose (HPC), poly(vinyl alcohol) (PVA) and sodium dodecylbenzenesulfonate (DBSNa). The effect of type and concentration of surfactant on the morphology have been investigated. Scanning electron microscopy was used to characterize the morphology of polyaniline. The results indicate that small and spherical nanoparticles can be obtained using PVA (6 g/L). Also better conductivity obtained when DBSNa (6 g/L) was used as surfactant. The chemical structure of products determined by fourier transform infrared spectroscopy (FTIR). The results show that the type of surface active agent affects the intensity of peaks.

Key Words: Polyaniline, Surfactant, Nanoparticles, Morphology, Chemical structure.

INTRODUCTION

Polyaniline (PAn) has been known for more than a century, since the synthesis of the so-called "aniline blacks" that enjoyed an early use as cotton dyes[1]. The synthesis of electroactive polymers have become two of the most important areas of research in materials science and polymer science during the past two decades[2-6]. Polyaniline can be synthesized by both electrochemical and chemical oxidative polymerization pathway[7]. Chemical synthesis has the advantage of being a simple process capable of producing bulk quantities of conductive polymer on a batch basis. To date, it has been the major commercial method of producing polyaniline. Several companies were produced bulk powders, dispersions and coated products[8].

The use of ammonium persulfate and potassium dichromate as oxidizing agent resulted in high yield, conductivity and viscosity of polyaniline. Potassium iodate and $FeCl_3$ have also given similar conductivity, but the viscosity of polyaniline was much lower. The use of $KMnO_4$ resulted poor conductivity of polymer. When $KClO_3$

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and $KBrO_3$ were use as oxidants the reaction rate and yield were low[9]. Armes *et al.*[10] utilized KIO_3 and concluded that substantial quantity of iodine is incorporated into the polymer matrix and leaches out when washed with organic solvents. Yasuda *et al.*[11] utilized $FeCl_3$ and Moon *et al.*[12] used H_2O_2-$FeSO_4$ for the preparation of polyaniline. However, yield and conductivity were not satisfactory. Sun *et al.*[13] prepared polyaniline with good conductivity (10 Scm^{-1}) and reasonable yield (60%) by using H_2O_2-Fe^{2+} system at 0-5 °C. Smith and coworkers conducted the polymerization of aniline in an emulsion of water and a non-polar or weakly polar organic solvent. This polymerization was carried out in presence of functionalized protonic acid such as dodecylbenzenesulfonic acid, which simultaneously acts as surfactant and protonating agent[14].

During the last decade, nanostructured (nanoparticles/-rods/-wires) conducting polyaniline with unusual physical and chemical properties have attracted great research interest. Much research has been conducted on the nanostructure of polyaniline (PAn) because it exhibits enhanced performance in applications where a high surface contact area is needed between the nanostructures and its environment. Recently, various strategies including template synthesis, interfacial polymerization, self-assembly and stepwise electrochemical deposition have been developed for the preparation of polyaniline nanostructures[15-18]. Although various methods of preparing PAn nanostructures have been reported, new simple and economical methods are still being explored.

In this work, polyaniline nanoparticles were prepared in water/tetrahydrofuran solution by chemical polymerization of aniline using KIO_3 as an oxidizing agent in the presence of various surfactants. Polyaniline nanoparticles were characterized by fourier transform infrared spectroscopy, scanning electron microscopy and conductivity measurements. Then the effect of surfactants on the colloidal morphology and electrical conductivity of suspension particles were considered.

EXPERIMENTAL

Morphologies of the products were obtained with a XL30 scanning electron microscope (SEM). Infrared spectra in the range 4000-400 cm^{-1} on the PAn sample pellets made with KBr were measured by means of an infrared spectrophotometer (Shimadzu 4100). The room temperature conductivity of compressed pellets was measured by a standard four-probe method using a Keithley 196 System DMM Digital Multi-meter and an Advantest R1642 programmable DC voltage/current generator as the current source.

Materials used in this work were: aniline monomer, sulfuric acid, tetrahydrofuran, potassium iodate, hydroxypropyl cellulose (HPC) (Mw = 10^6), poly(vinyl)-alcohol (PVA) (Mw = 72000), sodium dodecylbenzene sulfonate (DBSNa) from Merck. All reagents were used as received without further purification, unless stated otherwise. All of the aqueous solutions were prepared with distilled water. Aniline monomer was purified by simple distillation.

Synthesis of polyaniline: The reaction was carried out in water/tetrahydrofuran (50/50 % v/v) solution at room temperature for 5 h. In a typical experiment 1 mL aniline monomer was added to stirred aqueous solution of 50 mL 1 M sulfuric acid and 50 mL tetrahydrofuran containing 1 g of KIO_3 and 0.2 g HPC. After 5 h polymer was filtered, washed several times with deionized water to remove oligomers and other impurities. The polyaniline powder was dried at room temperature.

RESULTS AND DISCUSSION

Polyaniline salt containing mineral acid group as dopant by aqueous polymerization pathway is highly insoluble in organic solvents[19]. However, in the process for the preparation of polyaniline salt by emulsion polymerization pathway using dodecylbenzenesulfonic acid (DBSA) as surfactant, DBSA acts as surfactant as well as dopant for polyaniline salt[20]. This polyaniline salt containing DBSA as dopant is soluble in solvents and film can be obtained from the solution[21].

The polymerization reaction of aniline was carried out in water/tetrahydrofuran using different surfactants. The effect of type and concentration of surfactant were studied by using surfactant in the rang of (2-6 g/L). As can be seen in Figs. 1-5, the type of surfactant strongly influences the particle size and homogeneity of particles.
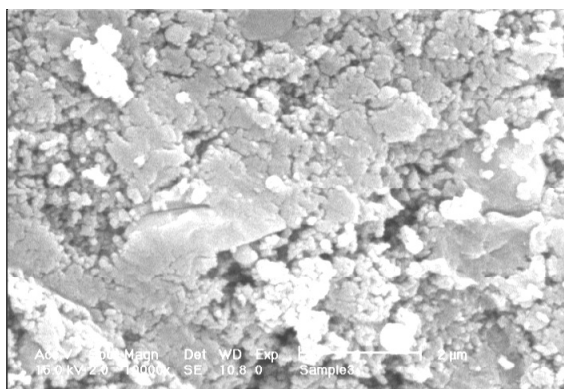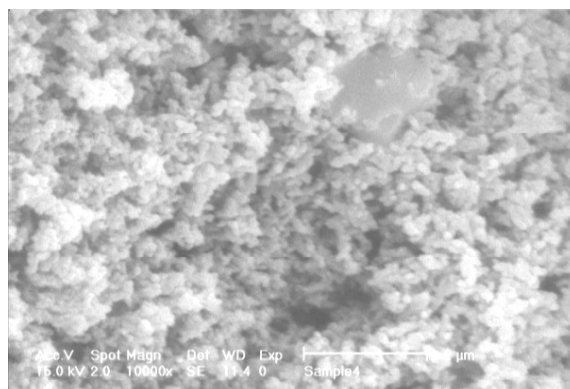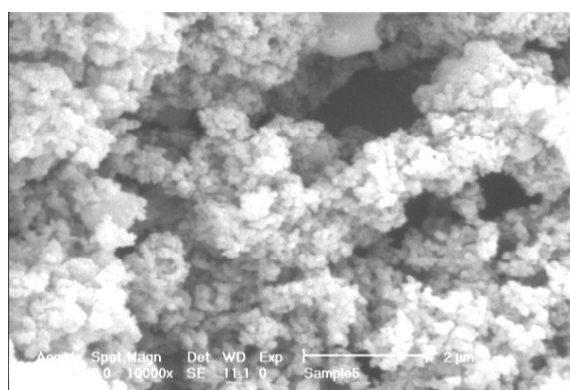

Fig. 1.   Scanning electron micrograph of polyaniline formed in aqueous/non-aqueous media. Reaction conditions: (KIO_3 = 10 g/L, aniline monomer 10.75×10^{-2} mol/L, volume of solution 100 mL, reaction time 5 h at room temperature)
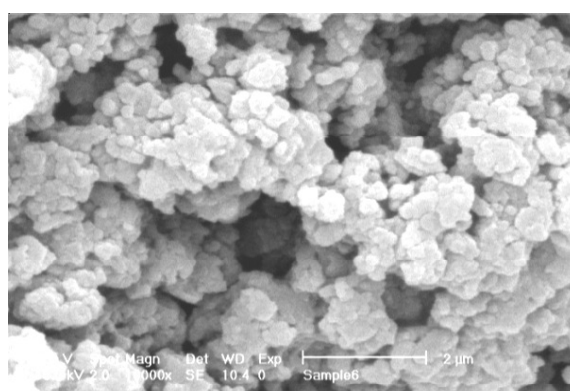
Fig. 1 shows the scanning electron micrograph of polyaniline formed in aqueous/non-aqueous media without any surfactant. As shown in Fig. 2b, polyaniline nanoparticles are observed obviously with diameter of *ca.* 100 nm and the shape of the polyaniline nanoparticles are very regular and uniform. Fig. 4a shows that the particles are linked and packed together, with diameter of 50-100 nm, which is very similar to the polyaniline nanoparticles prepared with the cationic surfactant (hexadecyl trimethyl ammonium bromide, HATB)[22]. The electrical conductivity of various composites produced under different reaction conditions was measured on
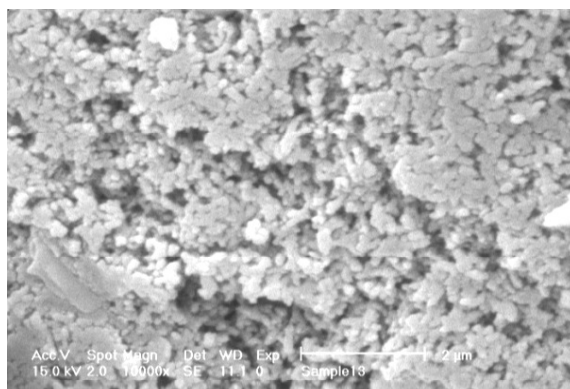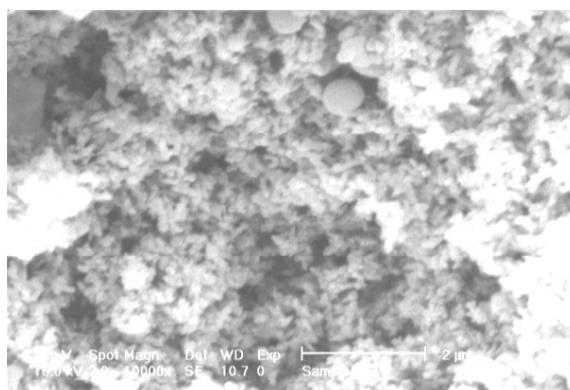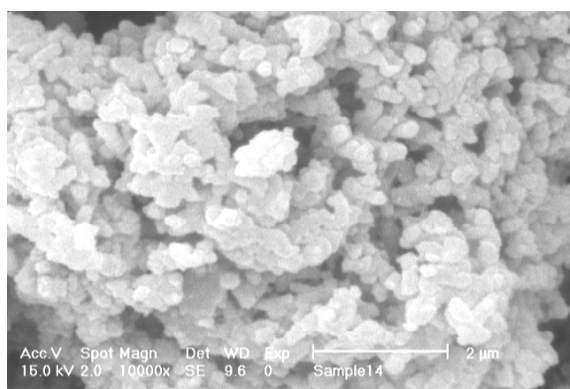
(a)

(b)

(c)

Fig. 2.   Scanning electron micrograph of polyaniline formed in aqueous/non-aqueous media. Reaction conditions: (KIO_3 = 10 g/L, aniline monomer 10.75×10^{-2} mol/L, volume of solution 100 mL, reaction time 5 h at room temperature), (a) PVA (2 g/L), (b) DBSNa (2 g/L) and (c) HPC (2 g/L) used as surfactant

(a)

(b)

(c)

Fig. 3.   Scanning electron micrograph of polyaniline formed in aqueous/non-aqueous media. Reaction conditions: (KIO_3 = 10 g/L, aniline monomer 10.75×10^{-2} mol/L, volume of solution 100 mL, reaction time 5 h at room temperature), (a) PVA (4 g/L), (b) DBSNa (4 g/L) and (c) HPC (4 g/L) used as surfactant
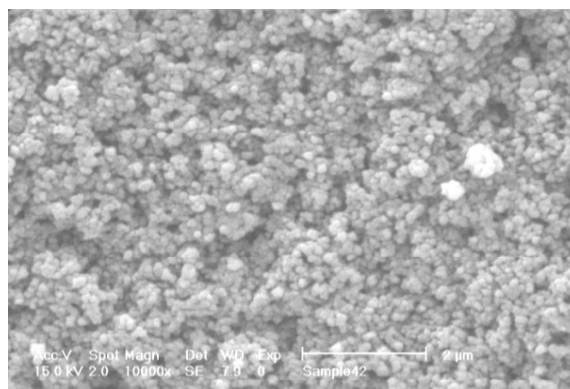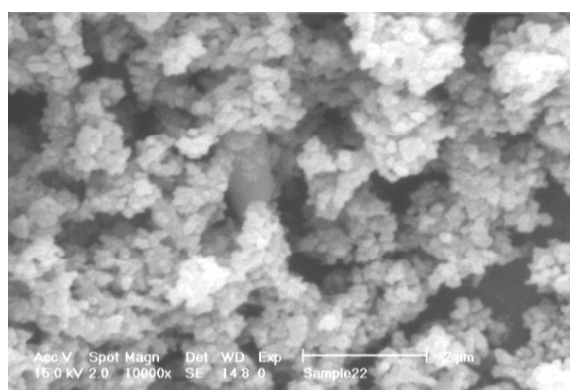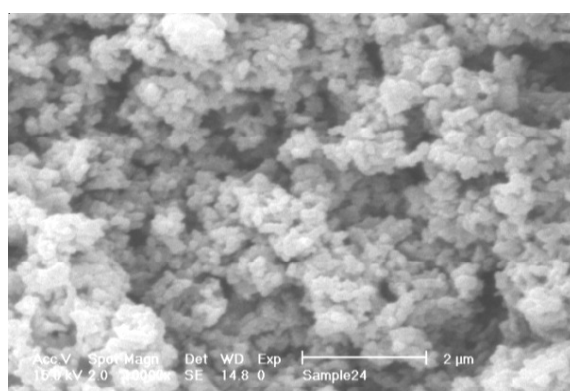
(a)

(b)

(c)

Fig. 4.   Scanning electron micrograph of polyaniline formed in aqueous/non-aqueous media. Reaction conditions: (KIO_3 = 10 g/L, aniline monomer 10.75×10^{-2} mol/L, volume of solution 100 mL, reaction time 5 h at room temperature), (a) PVA (6 g/L), (b) DBSNa (6 g/L) and (c) HPC (6 g/L) used as surfactant
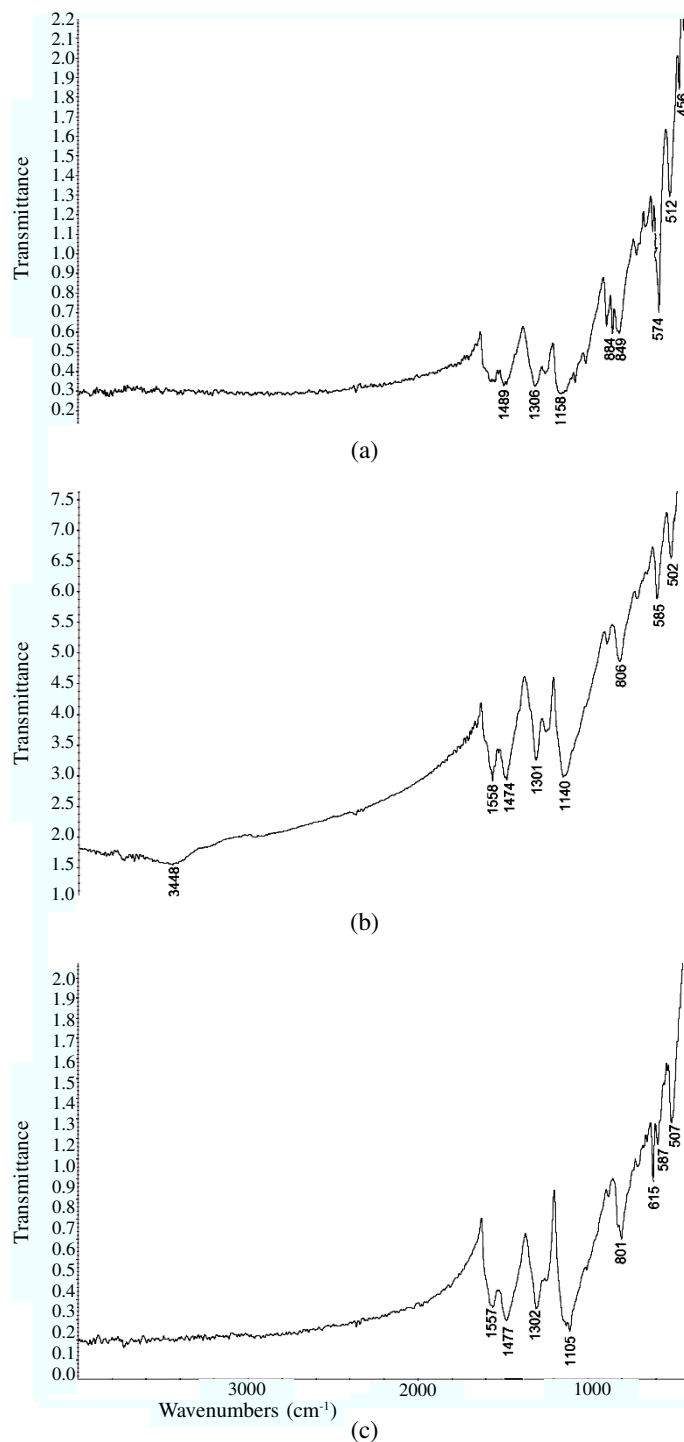
Fig. 5.   FTIR spectra of polyaniline formed in aqueous/nonaqueous media, (a) HPC, (b) PVA and (c) DBSNa used as surfactant

pressed pellets of the composite powders. The electrical conductivity of compressed pellets was measured using four point probe method. The results are shown in Table-1. When DBSNa used as surfactant, the conductivity increased from 2.1×10^{-3} to 8.2×10^{-2} when concentration of DBSNa varied from 2 to 6 g/L.

The uses of DBSNa, HPC and PVA as surfactants influence the conversion of monomer to polymer. As shown in Table-1, the yield of monomer to polymer decreased from 87 to 67 % when 0-6 g/L HPC was used as a surfactant. The effect of type and concentration of surfactant on the particle size are shown in Table-2. As can be seen particle size decreased when stabilizer concentration increased. By comparison between Figs. 3a and 4b, homogeneity increased by increasing stabilizer concentration.

TABLE-1
PREPARATION CONDITIONS AND TYPE OF SURFACTANT ON THE
CONDUCTIVITY AND CONVERSION OF MONOMER TO POLYMER

Type of solution	Type of surfactant	Concentration of surfactant (g/L)	Conversion of monomer to polymer (%)	Electrical conductivity (S/cm)
Water/tetrahydrofuran (50/50 % v/v)	–	–	87	2.1×10^{-3}
Water/tetrahydrofuran (50/50 % v/v)	DBSNa	2	54	6.5×10^{-3}
Water/tetrahydrofuran (50/50 % v/v)	HPC	2	79	1.3×10^{-3}
Water/tetrahydrofuran (50/50 % v/v)	PVA	2	73	1.4×10^{-3}
Water/tetrahydrofuran (50/50 % v/v)	DBSNa	4	61	3.4×10^{-2}
Water/tetrahydrofuran (50/50 % v/v)	HPC	4	72	5.7×10^{-4}
Water/tetrahydrofuran (50/50 % v/v)	PVA	4	71	1.6×10^{-3}
Water/tetrahydrofuran (50/50 % v/v)	DBSNa	6	57	8.2×10^{-2}
Water/tetrahydrofuran (50/50 % v/v)	HPC	6	67	1.7×10^{-4}
Water/tetrahydrofuran (50/50 % v/v)	PVA	6	69	1.0×10^{-3}

KIO_3 (10 g/L) used as an oxidant.

TABLE-2
PARTICLE SIZE OF POLYANILINE BY USING VARIOUS SURFACTANTS

Concentration (g/L)	Average particle size (nm) Type of surfactant		
	DBSNa	HPC	PVA
0	95	95	95
2	88	130	90
4	70	105	82
6	66	70	64

The chemical structure of obtained product was determined by FTIR spectrum. FTIR spectroscopy has provided valuable information regarding the formation of polyaniline. FTIR analysis has been done to identify the characteristic peaks of product. As can be seen in Fig. 5(b) polyaniline shows the presence of characteristic absorption bands at 1558 cm^{-1} (C=C stretching vibration of the quinoid ring), 1474 cm^{-1} (stretching vibration of C=C of the benzenoid ring), 1301 cm^{-1} (C-N stretching vibration), 1140 cm^{-1} (C-H in-plane deformation) and 806 cm^{-1} (C-H out-of-plane deformation).

Conclusion

The characteristics of polyaniline such as morphology, electrical conductivity, chemical structure and yield of monomer to polymer were investigated using various surfactants. It was found that, the type and concentration of surfactant have a considerable effect on the conductivity and morphology of resulting product. Particle size decreases and homogeneity increases when the concentration of surfactant increase. Nanospherical particles obtained when, 6 g/L PVA used as surfactant. The electrical conductivity increased by using DBSNa as a surfactant.

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