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Synthesis of Polyaniline Nanocomposites in Water/Ethyl Acetate Solution by Using Various Surfactants

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Polyaniline nanocomposites were prepared in the aqueous/non-aqueous media by using ammonium persulphate as an oxidant in the presence of various surfactants such as sodium dodecylbenzenesulfonate, poly(vinyl alcohol) and hydroxypropylcellulose. Polyaniline nanocomposites were characterized in terms of conductivity, morphology, yield, particle size and chemical structure. The results indicate that the morphology, yield, particle size and conductivity of products are dependent on the type of surfactant. Also, the structure of obtained product was determined by FTIR spectroscopy. The results show that the intensity of peaks is dependent on the type of surfactant.

Key Words: Polyaniline, Nanocomposites, Surfactant, Oxidant, Morphology, Chemical structure.

INTRODUCTION

During the last decades there has been widespread interest in conducting polymers. Polyaniline (PAn) is one of the most useful conducting polymers due to its ease of synthesis and environmental stability. It also has a wide range of electrical properties which can be easily controlled by changing its oxidation and protonation states[1,2]. However, there are still many unresolved problems concerning the structures and properties of polyaniline because of the complexities in molecular structure, due to synthesis conditions[3,4]. Improvement of polyaniline properties can be achieved either by forming composites and nanocomposites of aniline or blends with commercially available polymers or inorganic materials which offer better mechanical and optical properties, stability and processability[5-8].

Polyaniline which is soluble in common organic solvents have been synthesized by using organic acids of large molecular size or graft polymerization with poly-(aminostyrene)[9]. Stabilizer affects the morphology, particle size and conductivity of polyaniline. Particle size and conductivity can be decreased by increasing the concentration of stabilizer[10,11]. These are related to the mass of insulating stabilizer adsorbed.

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The insolubility in common solvents and infusibility of conducting polymers, in general, make them poorly processable, either by a solution technique or by melt processing methods[12,13]. Improvement of these material properties can be achieved by forming copolymers, composites, or blends with commercially available polymers or with inorganic materials which offer better mechanical and optical properties, stability, process ability[14].

The size and type of the dopant (anion) affect the morphology, size and electrical conductivity of resulting polymers[15,16]. The type and concentration of oxidant, type of protonic acids and additives affect the yield and electrical conductivity of polyaniline prepared chemically[17]. The polarity of the counter ion plays an important role in the conductivity as well as in the chemical properties. Conductivity increases which small counter ions are used[18]. The surfactants influence the physical properties (morphology, solubility, *etc.*) of the resultant polymer[19]. In this study polyaniline nanoparticles were prepared using various surfactants like sodium dodecylbenzenesulfonate (DBSNa), poly(vinyl alcohol) (PVA) and hydroxypropylcellulose (HPC). The products were characterized with FTIR, SEM and electrical conductivity measurement.

EXPERIMENTAL

A magnetic mixer model MK20, digital scale model FR 200, scanning electron microscope (SEM) model XL30 and fourier transform infrared (FTIR) spectrometer model Shimadzu 4100 were employed. The four point probe method was used to measure the volume resistivity of conducting polymer films.

Materials used in this study were aniline (Merck), hydroxypropylcellulose (HPC, $M_w = 10^6$) from Aldrich, sodium dodecylbenzenesulfonate (DBSNa) from Loba chemie, poly(vinyl alcohol) (PVA, $M_w = 72000$), sulfuric acid, ammonium persulphate from Merck. All reagents were used as received without further purification, unless stated otherwise. Distilled deionized water was used throughout this work. Aniline monomer was purified by simple distillation.

Polyaniline preparation: The reaction was carried out in aqueous/non-aqueous media at room temperature for 4 h. The conditions for polymer formation are listed in Table-1. In a typical experiment 1 mL aniline monomer was added to stirred aqueous solution (100 mL) of 1 M sulfuric acid containing 1 g ammonium persulphate. After 4 h, polymer was filtered, washed several times with deionized water and then dried in room temperature.

RESULTS AND DISCUSSION

Particle size and electrical conductivity of nanocomposite are listed in Table-1. As can be seen, particle size and electrical conductivity are dependent on the type of surfactant, because the surfactant bonded chemically (graft copolymer) to the growing polymer[20].

The electrical conductivities of various nanocomposites produced under different reaction conditions were measured on pressed pellets of the nanocomposite powders. The electrical conductivity of the compressed pellets was measured using four point

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

Type and concentration of surfactant (g/L)	Conversion of monomer to polymer (g)	Average particle size (nm)	Electrical conductivity (S/cm)
–	0. 69	–	3.5×10^{-4}
Dodecylbenzenesulfonate sodium = 3	0. 74	78	4.9×10^{-4}
Hydroxypropylcellulouse = 3	0. 65	121	2.7×10^{-4}
Poly(vinyl alcohol) = 3	0. 67	145	1.5×10^{-4}
Dodecylbenzenesulfonate sodium = 9	0. 76	81	8.6×10^{-6}
Hydroxypropylcellulouse = 9	0. 83	87	3.6×10^{-6}
Poly(vinyl alcohol) = 9	0. 72	109	2.3×10^{-7}

probe method. As can be seen in Table-1, the electrical conductivity of resultant products related to the type of surfactant. By comparison between DBSNa, HPC and PVA, conductivity increased using DBSNa, because DBSNa simultaneously acts as emulsifier and dopant. Also particle size related to the type of surfactant, due to surfactant prevent from gross aggregation of particles.

The surface morphology of polymers was studied using scanning electron microscope. As shown in Figs. 1-6, the size and homogeneity of particles dependent on the type of surfactant, because ionic and non-ionic additive influence the physical and chemical properties of solution and rate of polymerization.

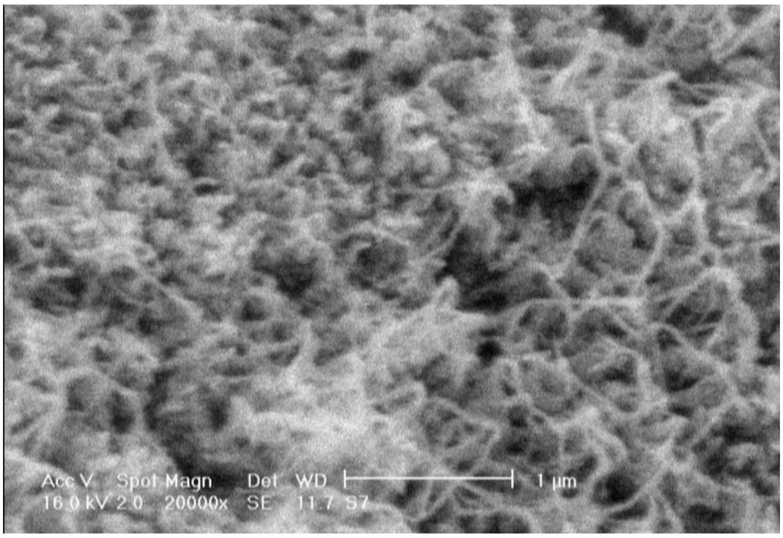

Fig. 1. Scanning electron micrograph of polyaniline in aqueous/non-aqueous (water/ethyl acetate) media. Reaction conditions: (ammonium persulphate = 10 g/L, aniline monomer 10.75×10^{-2} mol/L, volume of solution 100 mL (75/25 % v/v), reaction time 4 h at room temperature)

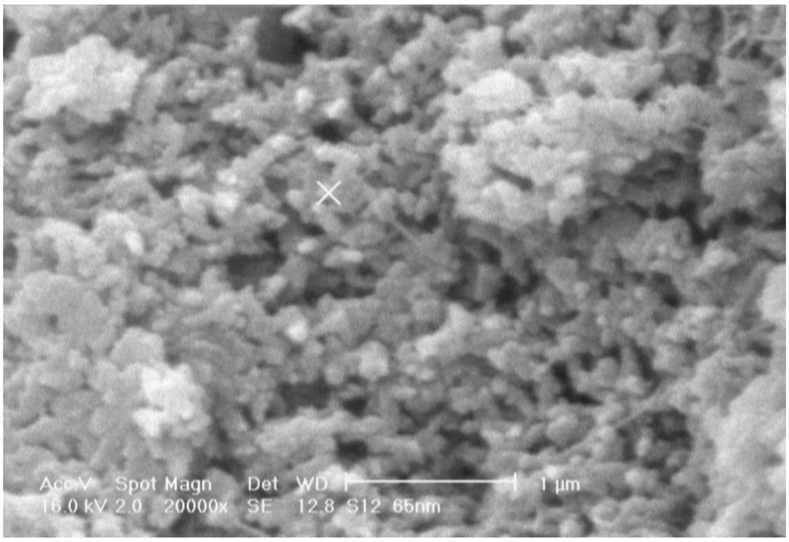

Fig. 2. Scanning electron micrograph of polyaniline in aqueous/non-aqueous (water/ethyl acetate) media. Reaction conditions: (ammonium persulphate = 10 g/L, aniline monomer 10.75 × 10^{-2} mol/L, sodium dodecylbenzenesulfonate = 3 g/L, volume of solution 100 mL (75/25 % v/v), reaction time 4 h at room temperature)

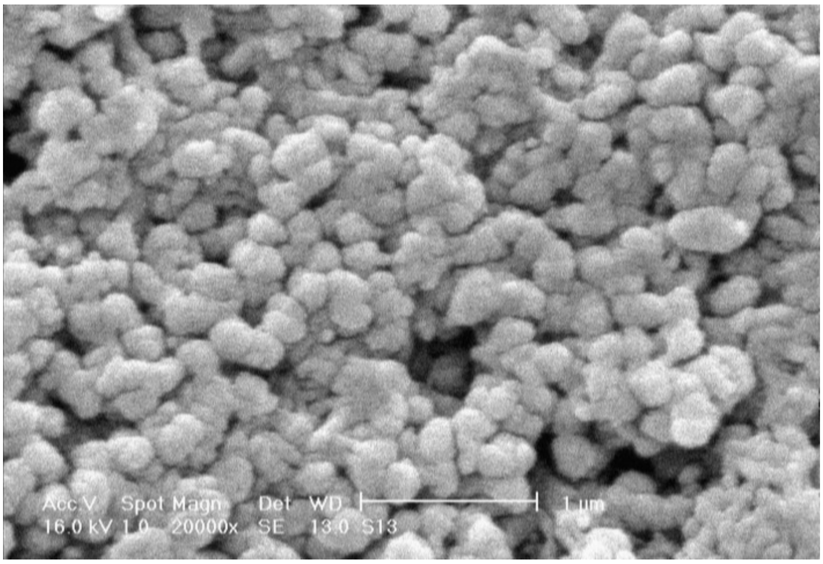

Fig. 3. Scanning electron micrograph of polyaniline in aqueous/non-aqueous (water/ethyl acetate) media. Reaction conditions: (ammonium persulphate = 10 g/L, aniline monomer 10.75 × 10^{-2} mol/L, poly(vinyl alcohol) = 3 g/L, volume of solution 100 mL (75/25 % v/v), reaction time 4 h at room temperature)

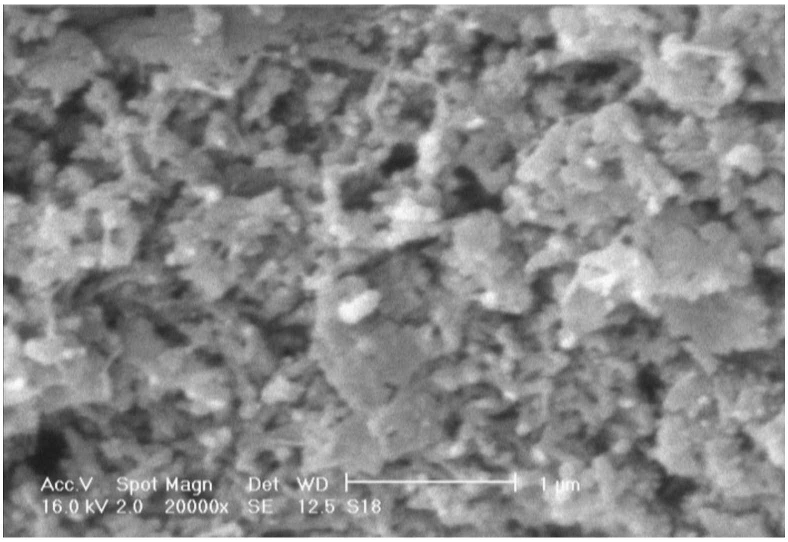

Fig. 4. Scanning electron micrograph of polyaniline in aqueous/non-aqueous (water/ethyl acetate) media. Reaction conditions: (ammonium persulphate = 10 g/L, aniline monomer 10.75 × 10^{-2} mol/L, sodium dodecylbenzenesulfonate = 9 g/L, volume of solution 100 mL (75/25 % v/v), reaction time 4 h at room temperature)

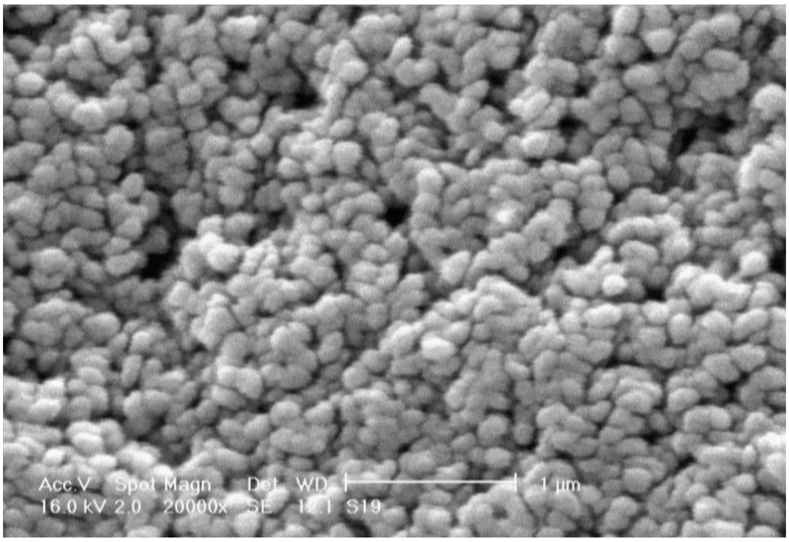

Fig. 5. Scanning electron micrograph of polyaniline in aqueous/non-aqueous (water/ethyl acetate) media. Reaction conditions: (ammonium persulphate = 10 g/L, aniline monomer 10.75 × 10^{-2} mol/L, poly(vinyl alcohol) = 9 g/L, volume of solution 100 mL (75/25 % v/v), reaction time 4 h at room temperature)

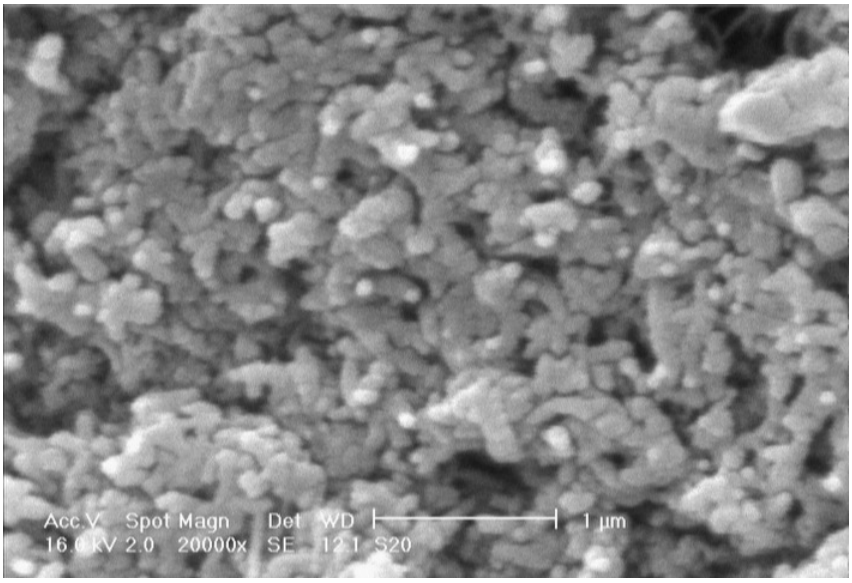

Fig. 6. Scanning electron micrograph of polyaniline inpolyaniline aqueous/non-aqueous (water/ ethyl acetate) media. Reaction conditions: (ammonium persulphate = 10 g/L, aniline monomer 10.75 × 10^{-2} mol/L, hydroxypropylcellulose = 9g/L, volume of solution 100 mL (75/25 % v/v), reaction time 4 h at room temperature)

The chemical structures of the obtained products were determined by FTIR spectroscopy. The FTIR spectra analysis has been done to identify the characteristic peaks of product. The FTIR spectra in the 2500-400 cm^{-1} region for various polymers are shown in Fig. 7. As can be seen, the FTIR spectrum changes when the composite is formed by polymerization. As shown in Fig. (7a), one characteristic of the aniline is unit at 1505 cm^{-1}. The peaks are at 1316 cm^{-1} (C-N stretching vibration), 1177 cm^{-1} (C-H in-plane deformation), 1007 cm^{-1} (N-H in-plane deformation) and 849 cm^{-1} (C-H out-of-plane deformation).

Conclusion

In this work, the characteristics of polyaniline nanocomposites such as morphology, electrical conductivity, chemical structure and yield of monomer to polymer were investigated. It was found that the type of surfactant has considerable effect on the conductivity, size, homogeneity, size distribution and morphology of resultant product which is probably due to additive absorption. As can be seen in Fig. 6, monodisperse spherical particles were obtained when PVA was used as surfactant. The structure of products was determined by FTIR spectrum. The results indicate that the intensity of peaks related to the type of surfactant.

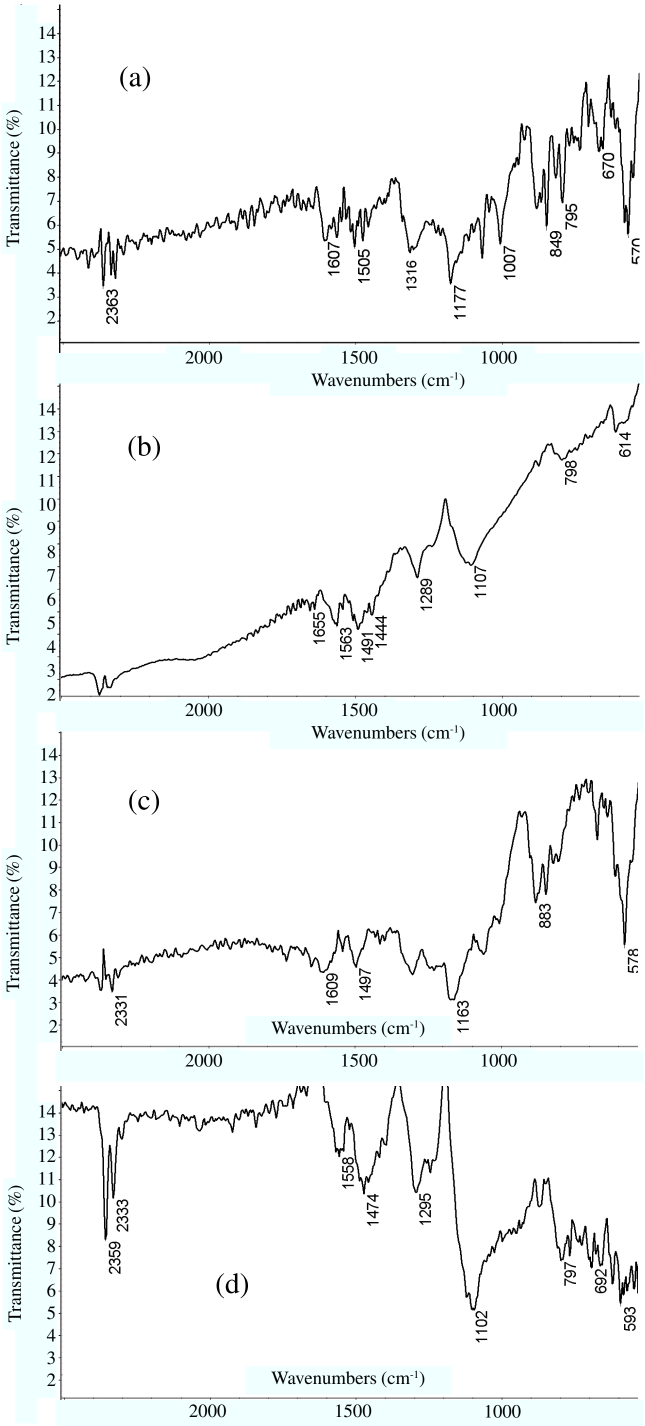

Fig. 7. FTIR spectra of (a) pure polyaniline without surfactant and with (b) DBSNa, (c) PVA and (d) HPC were used as surfactant

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